ENVIRONMENTAL POLLUTION STUDIES ON SURFACE ENTRAPMENT OF WATER POLLUTANTS ON ADSORBENTS

THESIS

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DEDICATED
TO My
BELOVED PARENTS

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CERTIFICATE

This is to certify that the work embodied in this thesis entitled "**Environmental Pollution-Studies on Surface Entrapment of Water Pollutants on Adsorbents**" is the original contribution of **Mr. Mohd. Rafatullah** and is suitable for submission for the award of Ph. D. degree in Chemistry of Aligarh Muslim University, Aligarh.

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LIST OF PUBLICATIONS

1. Sorption Studies for the Removal of Zn(II) and Cd(II) Ions on Treated Sawdust of Sissoo Wood. Anees Ahmad*, **Mohd. Rafatullah** and Md. Danish. *Holz als Roh und Werkstoff* (2007) Accepted.
2. Adsorption Dynamics and Equilibrium Studies of Heavy Metal Ions onto Mango Sawdust. Anees Ahmad*, **Mohd. Rafatullah** and Md. Danish. *Journal of Colloid and Interface Science* (2005) **Communicated**.
3. Comparative Studies on the Removal of Cu(II) Ions from Aqueous Solutions by using Different Adsorbents. Anees Ahmad*, **Mohd. Rafatullah** and Md. Danish. *Water Environment Research* (2005) **Communicated**.
4. Removal of As(III) from Aqueous Solutions through Adsorption on Activated Carbon. Anees Ahmad*, **Mohd. Rafatullah** and Md. Danish. *Journal of the Indian Council of Chemists* (2005) **Communicated**.

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ABSTRACT

ABSTRACT

Environmental Pollution is now an important problem in the whole world and a number of pollutants are causing havoc, owing to increased industrialization and population overflow, and much effort is directed towards its control. The pollutants are generally introduced into the environment as sewage, waste, accidental discharge or as a by-product of manufacturing processes. The pollutants may be broadly classified as inorganic and organic pollutants. They are found in all three states, viz. solid, liquid and gas. These pollutants are summarized in Chapter 1 and listed in table 1.1 and 1.2.

The presence of toxic heavy metals in industrial effluents such as zinc, cadmium, copper, chromium, nickel, lead, antimony, mercury, arsenic etc. has become a matter of environmental concern. Mining, tannery, jewelry, chemical, metallurgical, electrical and electronics large scale industries in industrial nations, and also arts and crafts in developing countries are the main sources causing heavy metal pollution. Use of different adsorbents, namely, sawdust, activated carbon, fly ash etc. is of current interest in the removal of heavy metals from water and wastewater. In recent years the use of adsorption technique for the removal of heavy metals from wastewater has received global attention and different substances have been employed as adsorbents.

The work described in the thesis deals with the studies on the adsorption behaviour of some heavy metals and their removal and documented in the following chapters:

Chapter-I- General introduction

Chapter-II- Sorption studies for the removal of Zn(II) and Cd(II) ions on treated sawdust of sissoo wood

Chapter-III- Adsorption dynamics and equilibrium studies of heavy metal ions onto mango sawdust

Chapter-IV- Comparative studies on the removal of Cu(II) ions from aqueous solutions by using different adsorbents

Chapter- V- Removal of As(III) from aqueous solutions through adsorption on activated carbon

Chapter I includes the literature survey on environmental pollution in general and water pollution in particular. It has a detailed literature on the latest work of different researchers on water pollutants, effect of water pollutants, heavy metal pollution and adsorption. The literature survey also includes the studies conducted by different workers on the adsorption properties of sawdust under the following headings:

- Adsorption of heavy metal ions
- Adsorption of phenolic compounds and alcohols
- Adsorption of hydrocarbons

- Adsorption of fats and oils
- Adsorption of dyes

Chapter II contains brief introduction on adsorption of Zn(II) and Cd(II) ions on sawdust of sissoo wood treated with formaldehyde. The effects of time of equilibrium, pH, temperatures and dosage of the adsorbent on the removal of Zn(II) and Cd(II) ions have been studied. The equilibrium nature of Zn(II) and Cd(II) ions adsorption at different temperature (25-60°C) has been studied. The percent adsorption of Zn(II) and Cd(II) ions increased with an increase in pH, temperature and dosage of treated sawdust. The adsorption followed Langmuir isotherms. The adsorption of Zn(II) and Cd(II) ions takes place in the order of Cd(II) > Zn(II). The applicability of Langmuir isotherm suggests the formation of monolayer coverage by Zn(II) and Cd(II) ions at the surface of the adsorbent. The thermodynamic parameters like free energy, enthalpy and entropy changes for the adsorption of Zn(II) and Cd(II) ions have also been computed and discussed. The heat of adsorption [ΔH_{Zn} = 17.706 kJmole^{-1} and ΔH_{Cd} = 16.949 kJmole^{-1}] implied that the adsorption process was endothermic in nature.

Chapter III describes the use of mango sawdust in the removal of Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solutions. The results obtained in this study demonstrated the potential use of mango sawdust for the removal of these metal ions from aqueous solutions. The kinetic studies indicated that equilibrium in the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions on sawdust was reached

within 120 minutes of contact between the sawdust and the solution. The different kinetics models viz. first-order reaction, a pseudo first-order and second-order reaction were simulated to fit the observed adsorption data. The second-order was found to be the best fit for these studies. Further the adsorption dynamic studies indicated that the rate of controlling step is mainly intraparticle diffusion but is not the only rate-limiting step for the metal ions. Batch adsorption studies shown that sawdust was able to adsorb Cu(II), Cr(III), Ni(II) and Pb(II) from aqueous solutions in the concentration range 100-1000 mgL^{-1}. The parameters studied include equilibrium time, temperature, and initial metal concentration of the adsorbate and dosage of adsorbent. The percent adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) increase with increase in concentration of adsorbate, dosage of adsorbent. The reaction rate for the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions increased with an increase in temperature. It was also observed that the adsorption process obeyed the Langmuir adsorption isotherms.

Chapter IV describe the adsorption technique using sissoo sawdust for the removal of Cu(II) ions from aqueous solutions. The results have also been compared with those of activated carbon and fly ash. The results showed that with in a contact time of 90 minutes about 82-86% of Cu(II) ions adsorbed in case of activated carbon and sawdust but in case of fly ash only 30% Cu(II) was adsorbed from solution in 120 minutes. The amount of Cu(II) ions adsorbed onto the different adsorbents increased with an increase in concentration and temperature.

The optimum pH corresponding to the maximum adsorption was found to lie at 6. The uptake capacity of the adsorbents was found in the order:

activated carbon > sissoo sawdust > fly ash

The optimum conditions for the removal have been worked out and the mechanism of the process is also discussed. Adsorption isotherm can be described by the Langmuir as well as Freundlich equations. The related parameters of Langmuir and Freundlich constants are listed in Table 4.2.

Chapter V describes the use of activated carbon as an adsorbent for the removal of arsenic(III) from aqueous solutions. The adsorption isotherms were analyzed to explain the sorption process of this system. The extent of adsorption increased along with an increase of activated carbon dosage. The Langmuir adsorption models appears to be the best fitted one. The equilibrium nature of arsenic(III) adsorption at different temperature (25°-60°C) has been described by the Langmuir isotherms and a tentative mechanism has been proposed. The related parameters for Langmuir constants are listed in Table 5.3. The thermodynamic parameter like free energy, entropy and enthalpy changes for the adsorption of arsenic(III) have also been computed and discussed and the values are listed in Table 5.4. The heat of adsorption [ΔH = -2.0316 kJmole^{-1} for Langmuir adsorption and ΔH = -9.575 kJmole^{-1} for Freundlich adsorption] implied that the adsorption was exothermic in nature.

CHAPTER – I

GENERAL INTRODUCTION

INTRODUCTION

Environmental problems and their control have received a great deal of interest and publicity now-a-days. The scientists have come to realize that this is very complex area while many advances have been made in recent years; much is yet to be learned concerning pollution. Environmental pollution [1] has been defined as "contamination of the earth's environment with materials that interfere with human health, the quality of life, or the natural functioning of ecosystems" or in other words "wrong substances in a wrong quantity in the wrong time and at the wrong place".

There are two types of the cause of pollution, natural and man-made. Natural pollution occurs naturally and won't cause excessive harm to our lives due to its regeneration ability, while the man-made pollution is caused by human activities, and hard to get rid of. The backbones of man-made pollution are human population and technology. Naturally human needs contact to the environment, we get resources from nature. This is for the sake of living. By the increase of human population, the contact is getting more intensive, of course, due to increase of the needs. And by the findings and development of new technologies, human can apply them to get the resources. And it's common that new technologies would bring their respective side effects besides their advantages. Pollution is a growing

pain. Pollution is not a problem that came suddenly from the sky; it's our fault and has been a part of our life through many years.

TYPES OF POLLUTION

There are many types of pollutions we are facing now a day. Some of them are as follows:

1. AIR POLLUTION

Air pollution is indication of disturbances to the composition of compounds in the atmosphere, as it may be summarized below:

- Excess emission of gases/vapors into atmosphere
- Saturation of chemical compounds/particulates
- Rate of dissipation is smaller than rate of absorption through various cycles (i.e. carbon and nitrogen cycle)
- Emergence of new chemical reactions of reactive and non-biodegradable compounds.
- Global warming, acid rain, smog and ozone depletion.

In relation to this, we may observe the cycle which involves in our daily lives: carbon and nitrogen cycle. These two cycles are the most important of all, regulating the composition of carbon and nitrogen of earth.

SOURCES

We can classify major sources that lead to air pollution to the following categories:

- motor vehicle exhaust
- heat and power generation facilities
- industrial processes
- auto manufacturing
- fertilizers plants
- building demolition
- solid waste disposal
- solvent evaporation
- volcanic eruption
- fuel production
- roadway construction
- electrical components manufacturing
- extraction of metals
- forest fires
- agriculture

2. WATER POLLUTION

Water pollution is contamination of water by foreign matter that deteriorates the quality of the water. Water pollution covers pollutions in liquid forms like ocean pollution and river pollution. As the term applies, liquid pollution occurs in the oceans, lakes, streams, rivers, underground water and bays, in short liquid-containing areas. It involves the release of toxic substances, pathogenic germs,

substances that require much oxygen to decompose, easy-soluble substances, radioactivity, etc. that becomes deposited upon the bottom and their accumulations will interfere with the condition of aquatic ecosystems. For example, the eutrophication: lack of oxygen in a water body caused by excessive algae growths because of enrichment of pollutants.

WATER CYCLE AND POLLUTION

Water cycle is, simply saying, the circulation of water in earth. In fact, the water in the earth's biosphere is used and reused again and again. This is called water cycle or continuous movement of water between the earth and the atmosphere. It involves the following mechanisms:

- Evaporation: changing of water from liquid to gas
- Transpiration: Release of water vapor from plant leaves
- Condensation: changing of vapor to liquid (cooled down)
- Precipitation: Water that returns to the earth (water droplets in clouds become large enough and there comes the rain).

According to the water cycle, naturally, water around us will be absorbed to the land (soil) and rivers will stream from the upstream to the downstream and released to the sea. In normal situation organic pollutants are biodegraded by microbes and converted to a form that brings benefits to the aquatic life. And for

the inorganic pollutants, in the same situation, don't bring too much hazards because they are widely dispersed and have almost no effect to the environment which they are released to. In a small scale, both inorganic and organic pollutants safely decompose throughout the stream, their concentration decrease in the sea, and they don't harm the sea ecosystem and its distribution. But in an excessive scale, communities in beach and estuary will be affected by the pollutants, and can heavily harm them.

SOURCES

We can classify major sources that lead to water pollution to the following categories:

- petroleum products
- synthetic agricultural chemicals
- heavy metals
- hazardous wastes
- excess organic matter
- sediment
- infectious organisms
- air pollution
- thermal pollution
- soil pollution

3. LAND POLLUTION

Revered to as soil pollution, land pollution involves the following mechanism:

- Deposition of solid waste
- Accumulation of non-biodegradable materials
- Toxification of chemicals into poisons
- Alteration of soil chemical composition (imbalance of chemical equilibrium to soil medium)

SOURCES

We can classify major sources that lead to land pollution to the following categories:

- agriculture
- mining and quarrying
- sewage sludge
- dredged spoils
- household
- demolitions and constructions
- industrial

4. NOISE POLLUTION

This particular pollution is ever increasing with due to the rise in the utilization of heavy duty machineries of industrial facilities and vehicles, synonymous to the increase in the standard of living in most countries. We make sounds practically every seconds of our day, but to extend it has reached an unfavorable high intensity which had cause many disturbances and irritation to others emotionally that has adverse effects on our daily activities.

SOURCES

We can classify major sources that lead to noise pollution to the following categories:

- road traffic noise
- air traffic
- rail traffic
- neighborhood and domestic noise
- incompatible land use
- industrial noises

5. RADIOACTIVE POLLUTION

The 40's was the era where the first nuclear bomb is being developed, and that's why it's called the nuclear era. However, nuclear energy has already researched

back since 1900. Nuclear era reached its greatest peak in the world war, by showing its massive ability of destroying things. Nuclear energy is a form of energy that's released by the splitting of atoms. Since scientists have found a way to make use of the energy, it has also been used to generate electricity. Nuclear energy has been recognized as a clean energy because it doesn't release pollutants such as CO_2 to the atmosphere after its reaction that could damage our environment. It's also known that nuclear energy has reduced the amount of greenhouse gas emission, reducing emissions of CO_2 for about 500 million metric tons of carbon. Despite the advantage of nuclear as a clean energy, the big concern is the waste resulted from nuclear reaction, which is a form of pollution, called radioactivity. Radioactivity is a form of radiation (a form of energy that travels through space). Some elements in this world are naturally radioactive while some others are made to be. Radioactivity is emitted when a radioactive element become unstable and begin to decay in the attempt to regain their molecular stability. When an element decays, it emits energy and small particles. If it's still radioactive, it will repeat the process, until it finally regains its molecular stability and stop decaying.

SOURCES

We can classify major sources that lead to radioactive pollution to the following categories:

- nuclear power plants
- nuclear weapon
- transportation
- disposal of nuclear waste
- uranium mining

6. THERMAL POLLUTION

This has become an increasing and the most current pollution, owing to the increasing call of globalization everywhere. Heat produced from industries is a major contribution to the pollution, much to the operation of the heavy industries which produces high amount of heat energy. As we will show a summary to the event of this pollution happening:

- Raw materials for productivity (organic and inorganic products)
- Undergo different chemical reactions with several process
- Excess heat energy is produced as a waste product
- Heat is released through into atmosphere (vapor) and reverie system (liquid).
- Increase of temperature of environmental system

SOURCES

We can classify major sources that lead to thermal pollution to the following categories:

- power plants creating electricity from fossil fuel
- water as a cooling agent in industrial facilities
- deforestation of the shoreline
- soil erosion

POLLUTANTS

The environmental pollution is the burning problem in the whole world and a number of pollutants are causing havoc. Therefore, a number of books have been written and international symposia [2-9] have been organized on this subject. Pollutants are any substances that under excessive quantity in a wrong place and a wrong time will cause impurity to the living environment. Simply put, they're the things that cause pollution. Pollutants can be chemicals, ashes, sediment, organisms, heat, radiation, etc. which if exposed to the living environment will cause bad effects.

WATER POLLUTANTS

NON-PERSISTENT (DEGRADABLE)

- domestic sewage
- fertilizers
- some industrial wastes

These compounds can be broken down by chemical reactions or by natural bacteria into simple, non-polluting substances such as carbon dioxide and nitrogen. The process can lead to low oxygen levels and eutrophication if the pollution load is high. But this damage is reversible.

PERSISTENT (DEGRADE SLOWLY)

- some pesticides (e.g., DDT, dieldrin)
- some leachate components from landfill sites (municipal, industrial)
- petroleum and petroleum products
- PCBs, dioxins, polyaromatic hydrocarbons (PAHs)
- radioactive materials such as strontium-90, cesium-137, radium-226, and uranium
- metals such as lead, mercury, cadmium

This is the most rapidly growing type of pollution and includes substances that degrade very slowly or cannot be broken down at all; they may remain in the aquatic environment for years or longer periods of time. The damage they cause is either irreversible or reparable only over decades or centuries.

OTHER

- warm water from cooling towers (thermal pollution)
- floating debris
- garbage
- foam

These are examples not of chemical pollution, but of physical pollution which interferes mainly with the usability and/or aesthetic appeal of the water.

In this section we have discussed some of common pollutants existing these days:

- Heavy metals
- Radioactive materials
- Biological pollutants
- Machineries
- Synthetic chemicals

EFFECT OF WATER POLLUTANTS

The impact of a pollutant depends upon its properties and amount. Pollutants bring about physical and chemical changes that make the water in rivers, lakes and ponds unfit for drinking and harmful to aquatic life. Some of the main effects of pollutants are mentioned below:

1. The biological effects of chemical pollutants are varied. Compounds of mercury, arsenic and lead are poisonous. Some compounds are so corrosive

that they may even affect waste treatment plants. Organic Sulphur compounds interfere with nitrification. Inorganic nitrates and phosphates stimulate excessive plant growth in lakes and reservoirs. The organochlorines from pesticides are highly persistent and pass through food chains. They mainly accumulate in fatty tissues and affect the nervous system. The broad spectrum pesticides used currently cause mass destruction of aquatic life through their accidental release or excessive use.

2. Change in colour is very common effect produced by the dyes, inorganic substances like chromium and iron compounds contained in the discharges.
3. Turbidity due to very fine suspended matter colloidal substances making water unfit for drinking and for industrial uses.
4. Impairment of test caused by industrial effluents containing iron, free chlorine, phenol, manganese detergents, oils, hydrocarbons and decomposition products. Unpleasant odours due to the presence of free chlorines, phenol, hydrogen sulphides, ammonia, algae and microorganisms.
5. Foam formation in waters by soaps detergents and alkalies.
6. Eutrophication is a natural process observed in lakes and tanks where the rich growth of microorganisms consumes much of the dissolved oxygen, tending to deprive other organisms. It is generally found at the bottom

layers of deep lakes. Addition of excessive plant nutrients intensify euterophication and are harmful to fish and other aquatic life.

The pollutants may be broadly classified as inorganic and organic pollutants. They are found in all three states, viz. solid, liquid and gas. These pollutants are summarized and listed in table 1.1 and 1.2.

Table-1.1

COMMON INORGANIC POLLUTANTS

S. No.	**Pollutants**	**Sources**	**Nature of Pollution**	**Remarks**
1.	Carbon monoxide	Incomplete combustion of carbon	Air	Leads to unconsciousness (300 ppm) and ultimately death (750 ppm)
2.	Carbon dioxide	Combustion of carbon from various sources	Air	Excessive CO_2 may lead to green house effect
3.	Sulphur dioxide	Oil refineries, thermal stations, fertilizer and sulphuric acid plants,	Air and water	Damage nucleic acids

		petroleum industries		
4.	Hydrogen sulphide	Decomposition of organic matter, sewage, petroleum industries and refineries	Air and water	Respiratory irritation in man, corrosion of materials, affects growing tips of sensitive plants
5.	Nitrogen oxide	Combustion process in air exhausts of automobiles, explosive industries	Air	Chronic respiratory ailments
6.	Lead	Exhaust of automobiles, jet engines artificial satellites	Air, water and soil	Lead compounds coagulated body proteins and seriously disrupt metabolic activities
7.	Zn, Hg, Cu, Ni, Cd,	Various industrial	Air, water	Mina Mata type of disease (Japan)

	Pb	discharges	and soil	
8.	Fluorides	Industrial waste	Water	Excessive of F^- leads to blackening of enamel or teeth
9.	Phosphates	Mainly from sewage of detergents	Water	Oxidative degradation of organic matter which consumes O_2
10.	Nitrates	Sewage	Water	Dissolved algal bloom, eutrophication of lakes, hamper fishing, navigation, irrigation and hydroelectric power
11.	Arsenic	Industrial waste liquors	Water and soil	Arsenic poisoning
12.	Cl_2, HCl	Industrial discharge	Air and Water	Respiratory ailments
13.	HCN and Cyanides	Steel plants, electroplating	Air, water and soil	Stops breathing, blood poisoning
14.	NH3 and ammonium compounds	Fertilizers industries biodegradation of pertinacious	Air, water and soil	Respiratory ailments, disrupt metabolic activities

		materials		
15.	Chromium	Effluent of planting and other metal processing factories	Water	Disrupt metabolic activities (70.05 ppm)

Table-1.2

COMMON ORGANIC POLLUTANTS

S. No.	**Pollutants**	**Sources**	**Nature of Pollution**	**Remarks**
1.	Organochlorine compounds e.g. DDT, BHC	Pesticides	Air, water and soil	Deposition in fat tissues, suspected carcinogens
2.	Organphosphorus e.g. Malathion, Monochrotophos	Pesticides	Air, water and soil	Carcinogen
3.	Carbamates e.g. Isolan, Dimetan, Pyramat	Pesticides	Air, water and soil	Inhibitor of cholin esterase

4.	Thiocyanates e.g. Lethane 60, Lethane 384	Pesticides	Air, water and soil	Interferes with cellular respiration and metabolism
5.	Formamides e.g. Chlordimeform, Amitraz	Pesticides	Air, water and soil	Carcinogen
6	Organosulphurs e.g. Tetradifon, Genite, Ovex	Pesticides	Air, water and soil	Comparatively less toxic and affects mites more
7.	Dinitrophenols e.g. Dinitrocresol, Morocide, Karathane	Pesticides	Air, water and soil	Causes rapid loss in weight
8.	Organotins e.g. Plictran	Pesticides	Air, water and soil	Inhibition of oxidative phosphrylation
9.	Organics containing tertiary nitrogen • Acridine • Atrazine	Pesticides Pesticides	Air, water and soil Air, water and soil	Carcinogen Carcinogen

	• Azobenzene	Pesticides	Air, water and soil	Liver injury
	• Bavistin	Pesticides	Air, water and soil	Carcinogen
	• Calixin	Coal, petroleum	Air, water and soil	Carcinogen
	• 2,4-Lutidine, and 2,6-Lutidine	Degradation of protein acious materials, bone oil	Air, water and soil	CNS depression, irritiation of skin and respiratory tract G. I. Disturbances, kidney and liver damage
	• Nicotinic acid	Tobacco	Air, water and soil	Carcinogen
	• Quinoline	Coaltar	Air, water and soil	Carcinogen
	• Picloram	Pesticide	Water	Carcinogen
	• Trimethylamine	Decay of fish	Water	Carcinogen

HEAVY METAL POLLUTION

Heavy metal readily accumulates through food web from producer to consumer. As it exceeds the maximum health standard level, it can be immediately poisonous or result in long-term health problems [10-11]. The gaseous products of fuel combustion from factories and automobiles contain particles of heavy metals, such as lead, zinc, cadmium, copper etc. Aluminium, chiefly extracted from bauxite is extensively used for canning, food packaging and as a foil for covering and preserving food stuffs. Workers in the mining and manufacturing industries may be exposed to particles of aluminium; contamination of the total environment with aluminium may result from the indiscriminate disposal of Al-containing products and wastes. Aluminium reduces the bioavailability of ATP and casein, and inhibits certain active enzymes by complexing them. Aluminium at 71.5 μg/ml in water causes anorexia, decreased activity, gill hyperplasia and mortality in fishes.

Various arsenic compounds, like lead arsenate, sodium and calcium arsenite salts are used as pesticide, monosodium arsenite and dimethyl arsenic acids are specifically employed as weed killers. Arsenic pollution of the environment results mainly from its release into air by the smelting of ores containing arsenic by combustion of coal and through the use of arsenical pesticides. The toxicity of arsenic lies in the fact that arsenites bind strongly with –SH groups of proteins resulting in enzyme inhibition. Arsenic induces skin lesions and lead to the development of skin cancer. Inorganic arsenicals act as lung

carcinogens in humans. Arsenites are very toxic to animals and plants. However, arsenic toxicity aquatic biota generally decreases with increasing pH of the medium due to the formation of its higher oxidation state. At much higher levels of exposure, arsenic induces hyperkeratosis, hyper pigmentation and neurological damage.

Cadmium occurs in air due to industries and human activities. Industries engaged in extraction, refining electroplating and welding of cadmium containing materials, and those in refining of copper, lead and zinc are the major source of cadmium in air. Cadmium is highly toxic because it does not exist homeostatic control in human body for this metal. The metal is known to accumulate in human liver and kidney. It causes hypertension, emphysema and kidney damage.

Wastes from leather tannins, explosive, ceramics, paint pigments, photography, wood preservation industrial units are a major source of water pollution by soluble chromate salts. Chromium in air is the result of fossil fuel burning and soil contamination by chromium results from the land disposal of slugs. The adverse effects of chromium are mainly associated with the hexavalent forms which are highly toxic to humans. It causes dermatitis, allergic skin reactions and gastro-intestinal ulcers.

Ingestion of excess amounts of cobalt causes polycystodemih in most mammals including man. Chronic exposure to cobalt at higher concentrations produces goiter.

The contamination of air with copper primarily results from its releases from the industrial units producing non-ferrous metals. Additional sources of atmospheric copper include wood combustion and steel production. Water pollution by copper results from the discharge of mine tailing and fly ash, which also forms the major source of solid copper contamination. Fertilizer production and disposal of industrial and municipal sewage wastes represent minor sources of copper in the environment. The ingestion of 15-75 mg of copper causes gastro-intestinal disturbances. The intake of large quantities of copper salts may cause hemolysis, hepatotoxic and nephrotoxic effects. Inhalation of airborne copper causes irritation of the respiratory tract and metal fume fever.

Iron is used in the production of machines, tools, paint pigments, building and bridge structure. Long term exposure to iron particularly Fe_2O_3 causes mottling of the lungs. Fe_2O_3 dust also serves as a co-carcinogenic substance.

Lead is the most ancient industrial position known to man. Lead arsenate is used in insecticide manufacture and escapes into the environment on application to plants. Lead compounds added to gasoline to reduce knocking are emitted into the air with the exhaust as volatile lead halides. Additional sources of exposure for children are the flakes of metallic lead in paint chips and soil, which may be ingested by them. Lead inhalation causes reduced hemoglobin formation, thus leading to anemia. Absorbed lead is deposited mostly in bones and in soft tissues and is a major source of brain damage, mental deficiency, headache, and abnormal

behaviour patterns. It can cause change in enzyme activity and even disturb the structure function relationship of DNA molecule. Inorganic lead affects the soil micro-organism by retarding the heterotrophic breakdown of organic matter.

Various human activities such as the use of mercury containing fungicides, paints and cosmetics release mercury in volatile form. Besides, the effluents from the plastic, chlor-alkali, electrical and electronic industries serve as a source of mercurial contamination of water. Mercury, in its inorganic form attacks mainly liver and kidneys, whereas organo-mercurials traverse the biological membranes and concentrate especially in the brain. It is also capable of inducing abortions and embryo toxic effects.

Smelting of ores contributes appreciably to the atmosphere levels of zinc. Municipal refuse and automobiles (tire weal, fuel-additives, brake linings and motor oils) serve as additional pollution sources. Agricultural use of $ZnSO_4$ containing pesticides and fungicides such as mancozeb, zineb and ziram are another important source of zinc in the environment. Zinc at concentrations over 15 mg/m^3 in air produces metal fume fever. Large dosage of zinc salts cause gastro-intestinal disorders including vomiting and diarrhea.

In developing country like India, there is an immense need of simple and inexpensive methods for pollution monitoring and control. Therefore, attempts have been made to develop simple and sensitive techniques for the detection and determine of these pollutant. Analytical chemistry plays a very important role in

both dealing and controlling environmental pollution. It can be thought as comprising of two branches, qualitative and quantitative. Qualitative analysis deals with finding what constitute or constituents are in analytical sample and quantitative analysis deals with the determination of how much of a given substance is in the sample. With today's instrumentation and with a large variety of chemical measurements available, specificity or sufficient selectivity can often be achieved so that the quantitative measurement serves as qualitative measurement.

Adsorption, ion exchange and chromatography are the important concepts in analytical chemistry, since the solid-liquid interactions have always been of interest because of their diversity and immense applications. Interactions between the components of liquids or solutions and surfaces of the solids make, in a wide variety of ways, a momentous contribution to our every day life. Its importance in the petroleum, chemical and pharmaceutical industries is well established. However, recent activities in biotechnology, medicine, biomedical, biochemical, environmental and polymer engineering have broadened the usefulness of these processes. An attempt has been made to report the developments made so for in the theory and practical on these aspect of study.

ADSORPTION

Adsorption [12] is a fundamental natural process since the molecules on the surface have an environment different from those in the bulk of material. The

surface has a different free energy from the bulk of the material. When he molecules of a gas or liquid are concentrated on the surface of a solid the molecules said to be adsorbed on the solid surface. So, adsorption may be defined, as "the phenomenon of higher concentration of any molecular species at the surface then in the bulk of a solid or a liquid is known as adsorption."

Adsorption can be distinguished from absorption. The adsorption is a surface phenomenon while absorption is a bulk phenomenon. In adsorption a substance is uniformly distributed through out the body of a solid or liquid. In adsorption solid that takes up a gas or vapour or a solute from a solution, is called the adsorbent, while the gas or the solute, which is held to the surface of the solid, is called the adsorbate. Mc. Bain [13] suggested that the term sorption should be used to describe a process in which both adsorption and absorption take place simultaneously.

Sometimes the adsorption can be classified as physical adsorption or physisorption and chemical adsorption or chemisorption. In physisorption the molecules are adsorbed on the solid surface by essentially the physical or Vander Wall's forces i.e., the forces of molecular attraction. A low heat of adsorption accompanies physical adsorption of a gas, which is of the same order as that of heat of liquefaction of gas. In chemisorption the gaseous molecules are more or less completely dissociated into atoms, which combine with the surface atoms of

the adsorbent by valence forces i.e., by the process of electron sharing as in the formation of chemical compounds. In chemisorption the surface enters in to reactions as a catalyst. This type of catalyst called heterogeneous catalysis is understandable only on the basis of some of the information deduced in adsorption studies. The photoelectron spectroscopy [ESCA] can be applied to reveal some of the binding properties of the adsorbed species. In surface studies this is normally referred as photoemission spectroscopy.

Adsorption is essentially a phenomenon of separating surface and the interfacial tension [14]. It is generally governed by the thermodynamic relation-

$$\Delta G = \Delta H - T\Delta S$$

ΔG, ΔH and ΔS are taken, respectively, as the free energy, heat and entropy changes in the process. The process of adsorption is generally exothermic but endothermic process has also been reported in case of large ionic-micelle (e. g. dyes) and some heavy metals.

The reverse process i. e. desorption measure the resistance of the system to change and manifests itself as binding force between the adsorbate and adsorbent. The binding forces involved may be of several types, such as Vander Waal's, ion exchange, covalent bond formation and hydrogen bonding depending on the nature of the substrate surface and the adsorbent. In the context of adsorption of polar compounds, it can be said that the binding forces are sorbate-substrate

bonds. Adsorption of the organic ions may then be controlled by Vander Waal's forces, electrical interactions like coulombic, dipole or hydrophobic interactions, operating on the uncharged groups of the ions (i. e. reversible) as well as by the electrical forces operating on the charged groups (chemical interaction, irreversible). When both the adsorbate and the adsorbents bear a charge, attractive forces can operate, and possibility of ion exchange cannot be ruled out.

The surface structure of a solid is controlled to a large extent, by the underlying bulk structure, which is defined by chemical composition, and crystal structure. The various surface group on the common polar adsorbents may ionize in the in the presence of water or similar solvents leaving a net charge on the solid surface is called zeta potential. This surface charge has been claimed by many workers [15-16] to have an important effect on the sorptive properties of an adsorbent, especially where ion exchange plays an important role.

ADSORPTION ISOTHERMS

Most of the studies on adsorption from solution have been concerned with equilibrium conditions and predominantly with the adsorption isotherms. An adsorption isotherm describes the equilibrium relationship between the adsorbed and unadsorbed sample, at a given temperature. It is a plot of the concentration of "X" in the adsorbed phase versus concentration of "X" in the unadsorbed phase. The interest in these isotherms lies in the amount of information they can yield, viz., identification of the adsorption mechanism, heat of adsorption, specific

surface area of the porous solid, diagnosis of the orientation of the solute molecules at the surface and its degree of self-association. There are four types of isotherms that are identified on the basis of the shape of the initial part of the isotherm. This classification by Giles et. al. [17] on the basis of solid-solution interface. Various shapes of the isotherms considered are shown in Figure 1.1 and can be characterized as follows-

- Langmuir or L-type isotherms
- S-type isotherms
- High affinity or H-type isotherms, and
- Constant partition or C-type isotherms

The L-type isotherms are most common. They are characterized by an initial region which is concave to the concentration axis. They are obtained when there is no strong competition from the solvent for sites on the surface. The curves refer to those cases in which the most active sites are initially covered, but the ease with which adsorption takes place decreases until a monolayer is completed.

For the S-type isotherms the initial region is convex to the concentration axis which is frequently followed by a point of inflection leading to an S-shaped curve. These isotherms indicate that-

1. The solvent is strongly adsorbed.
2. There is strong intermolecular attraction with in the adsorbed layer.
3. The adsorbate is monofunctional.

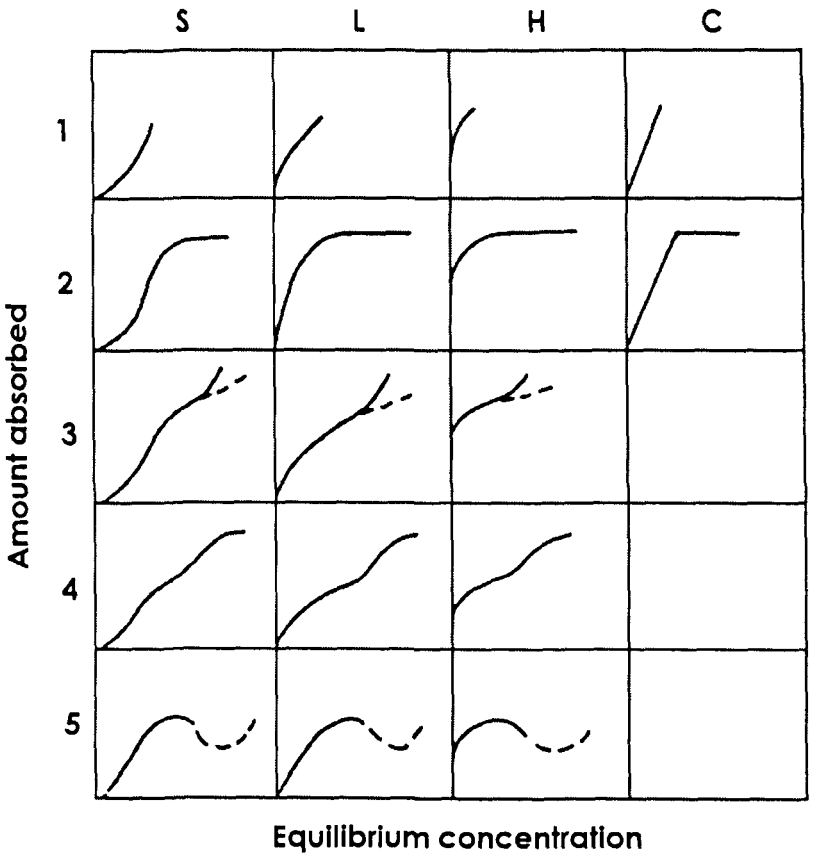


Figure 1.1:CLASSIFICATION OF ISOTHERM SHAPES

The second condition is most likely obtained if the major axis of the adsorbed molecules is perpendicular to the surface. By a monofunctional adsorbate we mean here that the molecule has a single point of strong attachment in an aromatic system or an aliphatic system of more then five carbon atoms. Further, the adsorbate is not miceller. In many cases, the S-curve indicates a 'cooperative adsorption' with solute molecules tending to be adsorbed packed in rows or clusters.

The H-curve occurs when there is a high affinity between the adsorbate and absorbent, which is shown even in very dilute solution. Thus, it can result from the chemisorption or from the adsorption of polymers or ionic micelles, through other special cases are also known.

Finally the C-type isotherm has an initial linear portion, which indicates a constant partition of the solute between the solution and the adsorbent and occurs with the microprobes adsorbents.

The isotherms have a great utility in diagnosing the mechanism of adsorption and also in distinguishing the probable configuration of the adsorbed molecules [17]. Thus, S-curve indicates a vertical orientation; L-curve shows the flat orientation and strong intermolecular interaction, while H-type isotherms are assumed to be typical of sample micelle formation. However, such a generalization needs great care, as many other factors also contribute to isotherms shape [18].

MECHANISM OF ADSORPTION

Although adsorption from solution by solids is of great practical importance and a large number of papers have been published. Much of the early work was concerned with relatively dilute solution, and interpretation of the isotherms was not unreasonably analogous to that used for adsorption from the gas phase and experimental results were fitted to equations of the Langmuir and Freundlich types. The role of solvent and its completion with the solute for surfaces sites has now become recognized as an important factor, particularly as a result of a large number of studies on the adsorption from binary liquid mixtures and their thermodynamic analysis.

The interaction between the surface and adsorbed species may be either chemical or physical. Several types of bonding and their examples can be identified as follows [19]-

1. **Chemical adsorption [chemisorption]**: - Steric acid from benzene solution on metal powders.
2. **Hydrogen bonding**: - Long-chain alcohols from hydrocarbon solution on dry oxide surfaces.
3. **Hydrophobic bonding**: -Association of hydrocarbon chains to "escape" from an aqueous environment, e.g. acids on polystyrene.

4. **Vander Wall's forces**: - The net interaction of adsorbate molecules with a surface might involve more than on the type of interaction, depending on the chemical structure of both components, e.g. adsorption of N_2 gas on activated carbon.

The most favoured approach to an investigation of the adsorption mechanism is a study of the isotherm. The important aspect are-

1. The rate of adsorption
2. The shape of isotherms
3. The significance of the plateau found in many isotherms
4. The extent of solvent adsorption
5. Whether the adsorption is monomolecular or multi layer
6. The orientation of the adsorbed molecules
7. The effect of temperature
8. The nature of the interaction between adsorbate and adsorbent

The adsorbents, which have been commonly studied earlier, are activated carbon [20-46], fly ash [47-68], peat [69-78], fibrous keratinous materials such as wool [79-81] and hair [82-84], clays [85-104], red mud [105-108], sludge [109-111], zeolite [112-123], biomass sorbents [124-134], inorganic adsorbents [135-139] etc. Some other adsorbents such as seed shell [140], sunflower stalk [141], Zea mays stalk [142], apple residues [143], coconut husk [144-145], tannin [146-147], gel sorbents [148-149], coffee residue [150], xanhate [151], cactus materials

[152-154], lignin [155], tea leaves [156-157], silica containing Iron(III) oxide [158], chitosan [159-162], rice husk [163-168] and bark [169-173].

STUDIES CONDUCTED BY DIFFERENT WORKERS ON THE ADSORPTION PROPERTIES OF SAWDUST

The numerous studies on the adsorption of different types of organic and inorganic pollutants on sawdust are summarized below-

ADSORPTION OF HEAVY METALS

Several authors have studies the fate of adsorption of heavy metals on sawdust. Tatsauaki et. al. [174] studied the application of sawdust for water treatment. Sawdust was treated with 0.01-0.1 N NaOH at 25-75C to remove lignin and to produce a porous adsorbent for removal of heavy metal from wastewater. The best result for Cu adsorption was by 15-50 mesh size and sawdust treated with 0.1 N NaOH for three cycles. Rikisaku et. al. [175] used the dye-treated sawdusts for removal of heavy metals from wastewater. Procoin-red or Procoin-yellow dyes treated sawdusts were highly effective for removal of many metal ions from aqueous solutions in batch and column experiments. Srivastava et. al. [176] used sawdust as an adsorbent for the removal of Cr^{6+} from industrial wastewater as CrO_4^{2-}. The adsorption of CrO_4^{2-} on to the sawdust was reported through chemisorption and remains unaffected by pH of effluent wastewater.

Bhargava et. al. [177] used sawdust for the removal of heavy metals (Cr, Pb and Cd) from synthetic wastewater by adsorption. The effect of metal

concentration, dosage of sawdust and the contact time were studied. The removal efficiency decreases at high metal concentration (>10 mg/L). It is observed that the order of extent of adsorption of these metal ions on sawdust is Cr > Pb > Cd. Timofeeva et. al. [178-179] used treated sawdust for the removal of heavy metals. The sawdust treated with an organic reagent. To improve the sorption capacity of the sawdust for Fe and Cr, 4, 7-bis (2-hydroxy-2-propyl)-2, 9-dimethyl-1, 5, 6-tritriacylcononane is used as the organic reagent. The sawdust and the organic reagent are taken in the ratio of 1: (0.5-1). He is also used the sorbent for removal of heavy metals from wastewater. In order to improve the sorption capacity of the sorbent, 1-(2-oxyethyl)-4, 5, 6, 7-tetrahydroindole is used as the reagent. The weight ratio of the sawdust to reagent being 1: (0.01-0.1).

Pilat et. al. [180] removed heavy metal ions from wastewater by filtering through a bed of sawdust (particle size 1.5 mm). The sawdust is pretreated with a 5-10 % solution of sodium and ammonium polysulfide at 90-400°C before filtration. The column of sawdust was used for the removal of Cr^{6+} from aqueous solutions by Singh et. al. [181]. They studied the effects of pH and concentration and reported the maximum removal of Cr^{6+} at pH 2. Vaishya and Prasad [182] have studied the adsorption of Cu(II) ions on sawdust of *Brassia latifollia* without any pH adjustment. Both Freundlich and Langmuir isotherm modeled the sorption equilibrium. The effect of pH was studied and maximum adsorption was observed at pH 7.3. Aval and Motedayan [183] also studied the adsorption behaviour of

Pb(II) and Cu(II) on sawdust. Shakila Begum [184] estimated Cu by using sawdust in effluents as well as in water with the help of Langmuir adsorption equation. The maximum adsorption capacity of the adsorbent increased with temperature between 30-50C. Chung et. al. [185] studied the adsorption behaviour of heavy metal ions on sawdust using columns.

Singh and Mishra [186] removed heavy metal ions using modified sawdust, which exhibits good adsorption potential for Hg^{2+}, Pb^{2+} and Cr^{6+}. Significant uptake of Ni^{2+}, Cd^{2+} and Cu^{2+} but is a poor scavenger for Zn^{2+} and Mn^{2+}. Adsorbent columns were used to remove Cr^{6+}, Hg^{2+} and Pb^{2+} from aqueous solutions. Doniec and andrzej [187] used active granular beds for removal of heavy metal ions from aqueous solutions. These granular beds made of aerated concrete containing fly ashes and cast Fe sawdust were used for elimination of heavy metals from aqueous solutions. High efficiency of removal of such metal as Cu and Pb was observed. Singh et. al. [188] studied the adsorption behaviour of sawdust of *Ficus benghensis* for the removal of Cr^{6+} from water and wastewater in the low pH range and reported 99 % removal of Cr^{6+} within 4.0 hrs. from wastewater. The ability of sawdust to adsorb Cr^{6+} from waste solution was studied in batch reactor under forced convection conditions by Mahmood et. al. [189]. Suteu et. al. [190] used agricultural wastes (bamboo and banana pulp, sawdust, jute, cotton, hemp) which have been successfully utilized for the removal of dyes and heavy metals from wastewater. Ajmal et. al. [191] studied the removal and

recovery of Cr^{6+} from electroplating waste by using pretreated sawdust. The sawdust was treated with disodium hydrogen phosphate. The adsorption process is pH dependent. They reported their studies on batch as well as by column processes. Raji et. al. [192] using the chemically modified sawdust in the removal of Pb(II) ions from aqueous media. The sorption of Pb(II) on polymerized sawdust has been found to be dependent on contact time, concentration, temperature, particle size and pH. Maximum removal of 98.6 % with 2.0 g/L of adsorbent was observed at 10.0 g/L adsorbate concentration, 6.0 pH and 60°C. The process follows first order kinetics with diffusion-controlled nature and the equilibrium data fit well with the Langmuir and Freundlich isotherms.

Raji et. al. [193] used sawdust based activated carbon for removal of heavy metal ions from water. The removal of Pb(II), Hg(II) and Cd(II) by activated carbon prepared from bicarbonate treated rubber wood sawdust is concentration, pH and temperature dependent. The percent adsorption of heavy metal ions increased with decrease in initial concentration of metal ions, increase in adsorbent dosage and temperature. The optimum pH for the removal of Pb(II) and Hg(II) is 4-8, where as maximum uptake for Cd(II) is at pH 5-9. The equilibrium data at different temperatures fit well with the Langmuir isotherm. Thermodynamics constant and standard free energy, enthalpy and entropy changes were calculated for predicting the nature of adsorption. Aoyama and Masakazu [194] used the polyphenols in forestry by-products (branches, leaves and sawdust) as adsorbent

for the removal and recovery of trace heavy metals in wastewater as well as feasibility studies of ginkgo and oak leaves. Chung et. al. [195] studied the adsorption and reduction characteristics of Cr(VI) by oak sawdust. The optimum adsorption condition was obtained from the measurement of the distribution coefficients (k_d) and adsorption capacity of Cr(VI) on the sawdust by changing pH of the solution. As a result, pH 2 was optimum because k_d of Cr(VI) was maximum and reducing quantity was minimum. Vorapanova et. al. [196] used the sawdust as both the reducing agent and adsorbent. Reduction of Cr(VI) to Cr(III) followed by adsorption is involved in the removal of Chromium from aqueous solution at acidic pH. Ajmal et. al. [197] used sawdust as an adsorbent for the removal of Cu(II) from wastewater for their safe disposal. The effects of contact time, pH, concentration, temperature, dosage, particle size of the adsorbent and salinity on the removal of Cu(II) have been studied. The equilibrium nature of Cu(II) adsorption at different temperatures (30-50°C) has been described by the Freundlich and Langmuir isotherm and a tentative mechanism has been proposed. The thermodynamic parameters like free energy, enthalpy and entropy changes for the adsorption of Cu(II) have also been computed and discussed.

Synthesis and use of esterified sawdusts bearing carboxyl group for the removal of Cd(II) from water was studied by Marchetti et. al. [198]. The reaction of succinic anhydride with wood meal was studied in order to preparation low cost materials for the removal of heavy metals. Without solvent, the use of one

equivalent of pyridine or triethylamine/succinic anhydride was necessary to obtain high grafting efficiencies at 80°C. In the presence of small quantities of 1, 2-dichloroethane as swelling agent, only 0.1 equivalent of catalyst was needed to obtain satisfactory results. Three more or less modified sawdusts were used after activation with $NaHCO_3$ for the removal of Cd(II) from water. Metal binding capacity was directly connected with the acid value esterified by titration and can reach 200 mg/g. Strongly modified sawdust showed a Cadmium binding capacity lower than expected because of diester formation. Reimert et. al. [199] studied the thermal conversion of sawdust in flow paths. The influences of reactor temperature (1050-1300°C), dust removal temperature (350-850°C), and gas atmosphere (oxidizing/reducing) on the distribution of heavy metals (from used sawdust) between slag and fly ashes during sawdust combustion in a flow path reactor were investigated. Under reducing conditions the limits for forest and agriculture of Pb, Zn, Cd and Cu in flying ashes were met at dust removal temperature > 800°C, whereas, the concentrations of Cr and Ni in the ashes were not affected whether by dust removal temperature nor by atmospheric conditions. Zhang et. al. [200] studied the removal of heavy metals from aqueous solutions by sawdust adsorption. He studied the sorption of Pb(II) on sawdust by batch techniques similar to the sorption of Cu(II). The equilibrium sorption level for Pb(II) is a function of solution pH, contact time, sorbent and sorbate concentration. The equilibrium adsorption capacity of sawdust for Pb(II) was

measured and extrapolated using linear Freundlich and Langmuir isotherms and compared with that for Cu(II). Metal ions, which are bonded to the sawdust, could be stripped by acidic solution so that the sawdust can be recycled. Non-equilibrium experiments were done by glass columns.

Removal of heavy metal cations from aqueous solutions by spruce sawdust has studied by Marin and Ayele [201]. The biosorption of metal ions Cd, Cu, Ni, Pb and Zn in single component solution and a multi component mixture in aqueous solution by spruce sawdust is reported. A comparative study performed through batch experiments between the cationic release of sawdust in ultra pure water and in a metallic solution leads to an understanding of the heavy metal ions fixation mechanism on sawdust. An empirical model is developed to distinguish between a sorption phenomenons purely based on ion exchange from one in which physical adsorption is involved. Thus difference in cation released between the two solutions corresponds to the metal ions, which bind to anionic sites by displacing protons from acidic group and existing cations from anionic sites. Metal ion binding capacities of spruce sawdust reach values ranging 2.1-4.3 times.10-2 meq/g in single metal ion solution with the following relative preferences-

$$Zn < Ni < Cd << Cu < Pb$$

A comparative study has done by Saravanane et. al. [202] for the removal of heavy metals from wastewater by using chemically modified low cost adsorbents. The removal efficiency of Cu(II), Mn(II), Fe(II), Ni(II), Pb(II) and

Zn(II) from wastewater by adsorption on non-convential materials and on chemically activated non-convential material is presented. The adsorption potential varied as a function of contact time, concentration, particle size, pH and flow rate. Chemically activated sawdust could remove Cu(II) 98.28 %, Mn(II) 100 %, Fe(II) 96.72 %, Cd(II) 96.72 %, Cr(III) 75 %, Ni(II) 80 %, Pb(II) 95 % and Zn(II) 93 % from the corresponding metal solution taken one at a time. Removal of some heavy metal cations from aqueous solution by spruce sawdust through column experiments has also done by Marin and Ayele [203]. The adsorption-desorption of Cu and a mixture of five metals Cd, Cu, Ni, Pb and Zn in aqueous solutions by a spruce sawdust column are reported. The use of column for Cu adsorption-desorption by successive cycles as well as the adsorption-desorption of a multi component solution were studied. An ion-exchange mechanism seemed to explain the removal of Cu by the natural components of sawdust, i.e. Ca, Mg and Mn accounting for 71, 13 and 5.5 % respectively, of the Cu binding on the sawdust. Regeneration of the sawdust column is described by the efficiency sequence: $H^+ > Ca^{2+} >> Na^+$, where protons were the most promising regenerating agent. Adsorption-desorption cycles showed that Cu binding capacity of sawdust, after a decrease of 23 % between cycles 1 and 2, was stabilized at 3.1 times 102 meq/g for the following cycles.

Meena et. al. [204] has studied the locally and commercially available adsorbents such as activated alumina, ion-exchange resin with special attention to

low cost adsorbents such as sawdust, treated sawdust and sand and to carry out a comparative study of their applicability to the removal of Cr and other heavy metal ions. Taty-Costodes et. al. [205] has removed the Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris*. Batch experiments were conducted to study the main parameters such as adsorbent concentration, initial adsorbate concentration, contact time, kinetic, pH solution and stirring velocity on the sorption of Cd(II) and Pb(II) ions by sawdust. The equilibrium of a solution between liquid and solid phases is described by Langmuir model. The capacity of the metal ions to bind onto the biomass was 96 % for Cd(II), and 98 % for Pb(II) ions. The adsorption of these heavy metals increased with the pH and reached a maximum at 5.5. Bulut and Tez [206] have studied the removal of heavy metal ions by modified sawdust of walnut. This adsorbent was found to be effective in removing Ni(II), Cd(II) and Pb(II) ions from aqueous solution. The equilibrium time was found to be about 60 minutes. The adsorption rate constant was calculated by kinetics, which fit a pseudo first order and second order laws. Experiments were carried out at three different temperatures expressed as both Freundlich and Langmuir isotherms. Freundlich and Langmuir constants as well as the thermodynamic parameters like free energy enthalpy and entropy change were calculated. Ho, Yuh-Shan [207] had written comment on removal of heavy metal ions by modified sawdust of walnut by Bulut, Y. and Tez, Z..

ADSORPTION OF PHENOLIC COMPOUNDS AND ALCOHOLS

Adsorption of phenolic compounds from aqueous solutions on sawdust has been reported in literature. Removal of phenolic compounds from water using impregnated sawdust was studied at 25°C by Singh et. al. [208]. They investigated the effect of pH on the recovery of these compounds from waste samples. Phenol removal from aqueous system by sorption on Jack wood sawdust was studied by Acharie et. al. [209]. The extent of removal depends on phenol concentration, pH of the solution and temperature. They reported the equilibrium time of 6 hrs. at pH 7, 62.5 percent removal was achieved at initial concentration 25 mg/L at 30°C. Geokchaev et. al. [210] studied the method for the removal of floating petroleum or petroleum product films from the surface of body of water by sorbent such as sawdust.

ADSORPTION OF HYDROCARBONS

Schoeller, Ferd [211] has studied the resin soaps and emulsions for dressing and finishing paper by using the sawdust or old paper by treatment with sulphonic acids of polynuclear aromatic hydrocarbons. Apell, Herbert R. [212] used treating sawdust for removal of arsenic from petroleum fractions. Tsushi, Heihachiro [213] used sawdust (moisture content 30 %) impregnated with paraffins vapour at 80°C for removing oil spills on water surface. Heavy oil (20 g) floating on water surface was removed by 10 g of the impregnated sawdust.

ADSORPTION OF FATS AND OILS

Kosugi, Kikuo [214] studied the animal wastes for production of fertilizer. Waste are homogenized, mixed with cyanamide, neutralized with H_3PO_4, H_2SO_4, HNO_3 and heated to < 60°C in an electrolysis tank using a. c. current. The treated material is separated into solids and liquids. The liquids after removal of oils and fats is mixed with sawdust to a moisture content of 60 % and the mixture is fermented yield a compost fertilizer. Lassmann et. al. [215] developed a method for removing halogenated organic compounds from wastewater. Animal or vegetable fats and oils are removed by adsorption using sawdust as an adsorbent by Mazet et. al. [216] from wastewater. Oda et. al. [217] studied the adsorption behaviour of sawdust-sandwiched mats for the removal of oils by adsorption. Oils and fats are easily and reliably removed from water containing oils and fats and the separated oils and fats can be used as a fuel studied by Yashima et. al. [218].

ADSORPTIONS OF DYES

Now-a-days dyes are also being removed from dying effluents by adsorption on sawdust. Many researchers have studied the use of sawdust for the adsorption of dyes. Asfour et. al. [219] used hard wood sawdust as an adsorbent for the adsorption of basic dye increased with decreasing particle size and increasing temperature. A. Nag [220] used charred sawdust as an adsorbent for the removal of dyes from water. Mazet et. al. [221] studied the removal of dyes from textile manufacture wastewater by sawdust from various tree species (beech, poplar,

birch, fir) as adsorbent. The adsorption behaviour of Cu^{2+}, Pb^{2+}, Hg^{2+} and Fe^{3+} ions on jute and sawdust dyed with several reactive dyes studied by Shukla and Sakhardande [222]. Dusart et. al. [223] studied the removal of dyes from wastewater using low cost materials such as peat, beech sawdust, charcoal and ion-exchange cellulosic papers. Suten et. al. [224] has studied the agricultural wastes (bamboo and banana pulp, sawdust, jute, cotton, hemp) which have been successfully utilized for the removal of dyes and heavy metals from wastewater. The possibility of using sawdust as an adsorbent in a fixed bed adsorber in depolarization of wastewater as well as batch wise studied by Mausi et. al. [225]. The adsorption follows Freundlich model adsorption for the adsorption of maxilin blue (basic dye stuff) on wood. Ibrahim et. al. [226] studied the removal of anionic dyes from aqueous solution by cellulose-based adsorbents. He also studied the removal of some commercial acid dyes from their aqueous solutions by anion exchange cellulosic-composite based on cross-linked wood sawdust bearing tertiary amino groups [227]. Khattri and Singh [228] studied the removal of dyes (crystal Violet, Methylene Blue, Malachite Green and Rhodamine B) from aqueous solutions at different concentrations, pH, and temperatures by Neem sawdust bioadsorbent. The percentage of the dyes adsorbed by Neem sawdust decreased from 91.56 to 78.94 and 84.93 to 71.25 for Crystal Violet and Malachite Green, respectively. Adsorption of other dyes (Methylene Blue and Rhodamine B) also decreased with increasing concentration of the dye in solutions. Marchetti et.

al. [229] studied the removal of anionic dyes from water by sawdust bearing quaternary ammonium groups as an adsorbent. Wang et. al. [230] studied the removal of dyes by using graft copolymers of sawdust as an adsorbent. Kadirvelu et. al. [231] studied the removal of dyes and heavy metal ions from aqueous solutions by using activated carbon prepared from the agricultural solid wastes, silk cotton hull, coconut tree sawdust, sago waste, maize cob and banana pith as an adsorbents. Results show all carbons were effective for the removal of pollutants from water. P. K. Malik [232] studied the removal of acid dyes from wastewater through activated carbon prepared from low cost Mahogany sawdust and rice husk utilized as the adsorbents. Results show that a pH of 3 is favorable for the adsorption of acid dyes. The adsorption capacities of sawdust carbon and rice husk carbon could be used as low cost alternatives to commercial activated carbon in wastewater treatment for the removal of acid dyes. Lim et. al. [233] has studied the removal of Reactive Blue 19 and Reactive Red 4 from aqueous solution by using quaternized sawdust modified with N-(3-Chloro-2-hydroxypropyl) trimethylammonium chloride an adsorbent. Removal of Acid Green 25 and Acid Red 183 from aqueous solutions by different adsorbent such as shells of almond and hazelnut, poplar and walnut sawdust was studied by Aydin et al. [234]. Capacities of adsorbent are walnut > poplar > almond > hazelnut for Acid Green 25 and almond > walnut > poplar > hazelnut for Acid Red 183. Jadhav and Vanjara [235-236] studied the removal of acidic, basic and disperse dyes from

dyestuff wastewater by using adsorbents such as sawdust, polymerized sawdust and sawdust carbon. Acidic and disperse dyes showed higher adsorption at higher pH whereas basic dyes showed higher adsorption at lower pH. Removal of direct dyes from spent textile dying wastewater through Mahogany sawdust carbon was studied by P. k. Malik [237]. Removal of basic dye (Methylene blue) from simulated wastewater by adsorption using Indian Rose wood sawdust was studied by Garg et. al. [238]. Ozacar et. al. [239] studied the removal of metal complex blue and metal complex yellow from aqueous solution by pine sawdust.

REFERENCES

1. A. K. De and B. K. Pal, *J. Indian Chem. Soc.*, **44**, 265 (1977).
2. I. Marr and M. S. Cresser, "*Environmental Chemical Analysis*", International text book, London (1993).
3. O. D. Tyagi and M. Mehra, "A Text Book of Environmental Chemistry", Ist Ed. (1990).
4. R. W. Peters, "*CSUI-ANL Conference on Issues in Water Management*", Argonne National Laboratory Oct. 25-26 (1990).
5. "*14th European Conference on Environmental Pollution, Aquatic and Atmospheric Environment-Air/Water Quality, Hazardous wastes Hydrology*", May 27-28, Helsinki, Finland (1993).
6. "*13th International Conference on Environmental Pollution and Hazardous Wastes*", June 17-18, Toronto, Canada (1993).
7. "*Regional Conference on Water Resources Management*", August 28-30, Isfahan, Iran (1995).
8. "*5th Stockholm Water Symposium*", August 13-18, Stockholm, Sweden (1995).
9. "*2nd Conference on Ecological Engineering for Waste Water Treatment*", September 18-22, Zurich, Switzerland (1995).

10. C. R. K. Murti and P. Vishwanathan, "*Environmental Contamination by Heavy Metals-Toxic Metals in the Indian Environment*", Tata-McGraw Hill, N. Delhi (1991).

11. J. E. Fergusson, "*The Heavy Elements Chemistry, the Environmental Impact and Health Effect*", Pergamon, Oxford (1990).

12. B. R. Puri and L. R. Sharma, "*Principle of Physical Chemistry*", p. 1010 (2003).

13. J. D. Seader and H. Henlay, Sep. Process. Principles, Wiley Publications, Singapore (1999).

14. A. W. Adamson, "*The Physical Chemistry of Surfaces, Inter Sciences*" (1960).

15. C. H. Giles, T. H. MacEwan, S. N. Nakhwa and D. Smith, *J. Chem. Soc.*, 3973 (1960).

16. C. H. Giles, I. A. Easton and R. B. Mcky, *J. Chem. Soc.*, 4495 (1964).

17. C. H. Giles, D. Smith and A. Huitson, *J. Colloid Interface Sci.*, **47**, 755 (1974).

18. L. R. Synder, "*Principles of Adsorption Chromatography*" Marcell Dekkar, p. 168 (1968).

19. G. D. Partfitt and C. H. Rochester, "*Adsorption from Solution at the Solid Liquid Interface*" p. 10 (1983).

20. W. Gen-Shuh, H. An-Tsun and G. Jnan-Xiaru, *Proc. Water Qual. Technol. Conf.*, 1996, 136-143 (Pub. 1997).

21. O. Eiji and I. Nabno, *Yokohama-shi kankyo kagaku kenkyosho*, **21**, 75-79 (1997).

22. El-Geundi and S. Mohammad, *Adsorpt. Sci. Technol.*, **15(10)**, 777-787 (1997).

23. Ye. Liyi, Zhong Hui and Zhang Huiping, *Xiamen Daxue Xuebao Ziran Kexueban*, **37(4)**, 542-546 (1998).

24. W. Angela, K. Annet and P. Kurt, *Acta Hydrochim. Hydrobiol.*, **26(1)**, 36-39 (1998).

25. G. Rolf and M. Hans-Joachim, *Biotechnol.* (2^{nd} Ed.)**11c**, 371-412 (2000).

26. C. Fangyan, T. Yubin and C. Jun, *Fushnu Shiyon Xueynan Xuebao*, **20(3)**, 26-29 (2000).

27. D. K. Singh and B. Srivastava, *J. Ind. Pollut. Control*, **16(1)**, 19-30 (2000).

28. K. Kadirvelu, K. Thamaraiselvi and C. Namasivayam, *Biresour. Technol.*, 2001, **76(1)**, 63-65 (Pub. 2000).

29. C. Faur-Brasquet, K. Kadirvelu and P. LeCloirec, *American Water Works Association,* 649-656 (2001).

30. L. R. Vanghan, and E. B. Reed, *American Water Works Association,* 1357-1371 (2001).

31. E. B. Reed, "*Environmental Separation of Heavy Metals*", 205-264 (2002).

32. R. Saravenane, T. Sundrarajan and R. S. Sivamurthy, *Ind. J. Environ. Health*, **44(2)**, 78-87 (2002).

33. L. Song-Yug and T. K. Ghosh, *Chemical Engg. Communications,* **189(4)**, 436-447 (2002).

34. T. Hisashi, Y. Hajimi, N. Toshiharu and M. Kazuyuki, *Jpn. Kokai Tokkyo Koho*, **9 pp**. (2002).

35. A. K. Krishnan and T. S. Anirudhan, *Industrial & Engineering chemistry Research*, **41(20)**, 5085-5093 (2002).

36. R. S. Amal and R. R. Srinivasa, *Ind. J. Environ. Prot.*, **22(1)**, 69-72 (2002).

37. E. A. Ashour, *Alexandria Engg. Journal*, **41(5)**, 867-873 (2002).

38. K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vemilamani and S. Pattabhi, *Biores. Technol.*, **87(1)**, 129-132 (2003).

39. K. K. Vasanth and K. Subanandan, *Chemical Industry Digest*, **16(1)**, 55-58 (2003).

40. R. R. Bansoda, J. N. Losso, W. E. Marshall, R. M. Rao and R. J. Portier, *Biores. Technol.*, **89(2)**, 115-119 (2003).

41. U. G. Beker, D. J. Malik, V. Strelko and M. Streat, *Chemical Engineering Communications*, **190(5-8)**, 610-629 (2003).

42. S. J. Park, Y. M. Kim and J. R. Lee, *Adsorpt. Sci. Technol.*, 437-441 (2003).

43. E. B. Reed, R. L. Vanghan and S. Edward, *Amirican Chemical Society, Division of Environmental Chemistry*, **43(2)**, 956-961 (2003).

44. C. Hulusi, L. Recep, A. Asude and I. Belgin, *Ekoloji: Cevre Dergisi*, **12(46)**, 38-42 (2003).

45. K. Santhy and P. Selvapathy, *Sep. Sci. Technol.*, **39(14)**, 3331-3351 (2004).

46. M. Chan-jun and L. Jung-heon, *Process Biochemistry* (Oxford, United Kingdom) **40(3-4)**, 1279-1283 (2004).

47. J. Shao, Z. Wang, H. Li and X. Shao, *Process Annual Int. Pittsburgh Coal Conf.*, 14th S15/16-S15/17 (1997).

48. K. Fytianos, E. Vondrias and A. Tsechpenakis, *J. Environ. Sci. Health, Part A, Environ. Sci. Engg. Toxic Hazard. Subst. Control*, **A32 (9 & 10)**, 2419-2427 (1997).

49. S. Jue-Fue, L. Suen-Zone, Y. Ying-Hsieu and L. Wen-Bing, *Zhongguo Huanjing Gongcheng Xuekau*, **7(3)**, 309-317 (1997).

50. A. K. De, *J. Inst. Chem.* (India) **69(6)**, 185-186 (1997).

51. Yau Cunxian and Tau Kui, *Shanghi Huanjing Kexue,* **16(7)**, 30-33 (1997).

52. V. K. Gupta, D. Mohan and S. Sharma, *Sep. Sci. Technol.*, **33(9)**, 1331-1343 (1998).

53. V. K. Gupta, S. Sharma, I. S. Yadav and D. Mohan, *J. Chem. Technol. Biotechnol.*, **71(2)**, 180-186 (1998).

54. G. Gupta and N. Torres, *J. Hazard. Mater.*, **57(1-3)**, 243-248 (1998).

55. Yu, Yanzhen, Li, Guozhong, Fu, Xinghua and Hon, Xianqin, *Guisuanyan Tongbao,* **17(3),** 42-45 (1998).

56. J. Ayala, F. Blanco, P. Garcia, P. Rodrignez and J. Sancho, *Fuel,* **77(11),** 1147-1154 (1998).

57. P. Ricon, I. Leeuyer, P. LeCloirec, *Watre Sci. Technol.*, **39(10-11),** 239-247 (1999).

58. A. K. De, *J. Inst. Chem.*, **71(6),** 237-238 (1999).

59. Wu Xiang-Yang and Yang Liu-Qing, *Jiangsu Ligong Daxue Xuebao,* **21(4),** 48-51 (2000).

60. G. Yongiong, W. Yanxin and C. Hesteng, *Gougye Shuichuli,* **21(12),** 9-12, 16 (2001).

61. C. Hee-Chan and O. Dal-Yong, *Chawon Rissaikuring,* **10(4),** 10-17 (2002).

62. K. V. Kumar, *Research journal of Chemistry and Environment,* **6(4),** 61-65 (2002).

63. B. Bayat, *Water Air and Soil Pollut.*, **136,** 69-92 (2002).

64. A. Doniec, M. Werecka and W. Gaz, *i Technika Sanitarua,* **76(8),** 292-295 (2002).

65. N. G. Vyazova, V. N. Krynkova and V. P. Latyshev, *Khimiya Tverdogo Topliva*, **3,** 82-86 (2003).

66. M. Rao, A. V. Parwate, A. G. Bhole and P. A. Kadu *Journal of Water supply: Research and Technol-AQUA*, **52(1),** 49-58 (2003).

67. P. Janos, H. Buchlova and M. Ryznasova, *Water Research,* **37(20)**, 4938-4944 (2003).

68. A. K. De, *Chemical and Environmental Research*, **12(1 & 2)**, 31-36 (2003).

69. T. Viraraghavan, R. Sapack and A. K. G. Rao, *Proc. Ann. Conv-West. Can. Water Wastewater Association*, **42**, 85-91 (1990).

70. J. S. D'Avila, C. M. Matos and M. R. Cavalcanti, *Water Sci. Technol.*, **26(9-11)**, 2309-2312 (1992).

71. S. V. Kertman, G. M. Kartman and Z. S. Chibrikova, *Zhurnal Prikladnoi Khimii* **66(2)**, 465-476 (1993).

72. T. Viraraghavan, M. J. Dronamra and M. Murali, *J. Environ. Sci. Health Part A*, **28(6)**, 1261-76 (1993).

73. T. Viraraghavan and A. K. G. Rao, *Int. J. Environ. Stud.*, **44(1)**, 9-27 (1993).

74. D. C. Sharma and C. F. Forster, *Water Research*, **27**, 1201 (1993).

75. L. B. Nanmova, N. P. Gorlenko and Z. I. Otmakohova, *Zhurnal Prikladnoi Khimii,* **68(9)**, 1461-65 (1995).

76. T. Matterer, B. MecArthy and R. Adams, *Mining Engineering*, **48(1)**, 53-56 (1996).

77. V. M. Dudarchik, T. V. Sokolova, T. P. Smychnik and V. S. Pekhtereva, *Vestsi Natsyyanal"nai Akademii Navuk Belarusi,* **(2)**, 95-99 (2003).

78. Q. Y. Sun, P. Lu and L. Z. Yang, *Environmental Geochemistry and Health*, **26(2-3)**, 311-317 (2004).

79. T. Matsuda, M. Takahashi, K. Shinoda and T. Kikyo, *Jpn. Kokai Tokkyo Koho*, 4pp.

80. D. Balkosa and H. Battacioghu, *J. Chemical Technol. Biotechnol.*, **54(4)**, 393-97 (1992).

81. W. Yuen-Huen, L. Su-Hsia and J. Ruey-Shin, *J. Hazards. Materials*, **102(2-3)**, 291-302 (2003).

82. S. S. Krishnan, A. Cancilla and R. E. Jervis, *J. Radioanaly. Nucl. Chem.*, **110(2)**, 373-78 (1987).

83. N. Balasubramanian, R. E. Raja, K. Lalitha and S. Prebha, *Asian J. Chem.*, **10(1)**, 136-145 (1998).

84. M. G. Prodauchuk, O. V. Gudz, O. M. Poik and O. O. Khudaikluva, *Khimichava Promislovist Ukraini*, **(2)**, 21-24 (2004).

85. C. Fernando, R. Rais and P. W. Robert, *Hazar. Ind. Waste*, **22**, 77-94 (1990).

86. K. P. Yadav, B. S. Tyagi and V. N. Singh, *J. Chem. Technol. Biotechnol.*, **51(1)**, 47-60 (1991).

87. V. M. Knatko and E. V. Shcherbakova, *Russ. Ru. Appl.*, (1993).

88. J. Bhatt, H.M. Mody and H. C. Bajaj, *Clay Res.*, **15(2)**, 28-32 (1996).

89. H. Yung-Chien, L. Yi-Hua and J. Hung-Yih, *Zhongguo Huanjing Gongcheng Xuekeu,* **7(4)**, 367-375 (1997).

90. C. Chun-Chiao and H. Yung-Chien, *Jiemian Kexue Huizhi*, **20(4)**, 215-223 (1997).

91. R. Chakravarty, G. Prasad and D. C. Ranpeinwar, *Environ. Technol.*, **19(3)**, 315-322 (1998).

92. X. Shen, S. Chen, Ye. Wang, Yimin Wang and W. Cai, *Huanjing Wuran Yu Fongzhi,* **20(3)**, 15-18 (1998).

93. V. P. Simeonova, *Water Supply*, **18(1/2)**, 636-640 (2000).

94. F. Barbier, G. Duc, M. Petit-Ramel, *Colloids Surf. A*, **166(1-3)**, 153-159 (A 2000).

95. C. Rafael, H. M. Carmen and C. Jnau, *Environ. Sci. Technol.*, **34(21)**, 4593-4599 (2000).

96. Z. Lizhong, W. Qing and C. Baoliang, *Huanjing Kexue*, **21(4)**, 42-46 (2000).

97. Anon Germany, *WLB Wasser, Luft Boden*, **44(9)**, 45 (2000).

98. Chen Tian-Hu, *Gaoxiao Dizhi Xuebao*, **6(2)**, 265-270 (2000).

99. W. L. Ijdo and T. J. Pinnavaia, *Green Chemistry*, **3(1)**, 10-12 (2001).

100. M. Hadan and M. Gutamann, *Ger. Offen.*, **5pp**.

101. G. W. Beall, *PCT. Int. Appl.* **70 pp**.

102. G. Alther, *Contaminated Soils*, **7**, 223-231 (2002).

103. P. A. Marques, R. Monica, N. A. Cardoso and S. G. A. Wagner, *Quimica Nova*, **25(6B)**, 1145-1154 (2002).

104. V. Boonamnuayvitaya, C. Chaiya, W. Tanthapanichakoon and S. Jarudilokkul, *Separation and Purification Technol.*, **35**, 11-22 (2004).

105. E. Lopez, B. Soto, M. Arias, A. Nunez, D. Rubinos and M. T. Barral, *Water Res.*, **32(4)**, 1314-1322 (1998).

106. C. Namasivayam and K. Thamaraiselvi, *Fresenius Environ. Bull.*, **7(5/6)**, 314-319 (1998).

107. K. Jung-Sik, H. Sang-Won, H. In-Gook, B. Jae-Heum and C. Woo-Zin, *Chawon Rissaikuring*, **9(1)**, 44-51 (2000).

108. R. Apek, E. Tuten, M. Hugul and M. Hizal, *Water Res.*, **32**, 430-440 (1998).

109. F. A. Lopez, C. Perez and A. Lopez-Delgedo, *J. Mater. Sci. Lett.*, **15(15)**, 1310-1312 (1996).

110. K. Selvaraj and V.C. Mohan, *J. Sci. Ind. Res.* **56(11)**, 673-679 (1997).

111. W. Chung-Hsin, L. Cheng-Lin and H. Pay-Yu, *J. Environ. Sci. Health A*, **39(1)**, 237-252 (2004).

112. Y. T. Yuan, *Ger. Offen. D. E.* **4**, 116, 890 (1991).

113. I. J. Lin and I. Spevakova, Prog. Miner. Process. Technol., *Proc. Int. Miner. Process.* 5th, 289-294 (1994).

114. B. K. T. Burggraef, G. m. b. H., *Austrian AT Appl.* (1996).

115. T. Marnyama and K. Morita, *Jpn. Kokai Tokkyo Koho*, **5pp**. (1997).

116. S. Priggesmeyer, S. Priggesmeyer, W. Hasmischmacher, H. Runde and G. Weil, Eur. Pat. Appl. Ep.1013611, **10 pp**. (1998).

117. K. Wada and T. Mineo, *Jpn. Kokai Tokkyo Koho Jp*, **5pp**. (1998).

118. I. Jun and Y. Akinori, T. Hiroyuki and T. Shigeyuki, *Jpn. Kokai Tokkyo Koho*, **7pp**. (1998).

119. V. W. Lutz, R. Bertram, W. Wieker and M. Jank, *Freiberg Forschungsh*, **A859**, 256-260 (A2000).

120. T. Mamoru and I. Hideaki, *Eco. Ind.*, **5(9)**, 25-30 (2000).

121. S. Sang-Kwon, P. Jin-Tai and K. Tal-San, *Anal. Sci. Technol.*, **13(1)**, 96-100 (2000).

122. A. Gladysz-Plaska, M. Kowalska-Terues, M. Majden, *Prezem. Chem.*, **79(9)**, 298-301 (2000).

123. S. Siddhesh, F. Robert, K. Phil and W. John, *American Chemical Society, Division of Environmental Chemistry*, **43(2)**, 367-369 (2003).

124. S. Li, C. Yi and D. Zhang, *Tam. Junjie*, **28(2)**, 261-264 (1991).

125. N. MAzied and K. Tulin, *Kim-Kim. Muhendisligi Sep.* 8th, **4**, 283-287 (1992).

126. S. Yasim, O. Dursun and K. Tulin, *Kim-Kim. Muhendisligi Sep.* 8th, **4**, 289-294 (1992).

127. K. M. Peknikar, P. R. Puranik, A. D. Agate and S. R. Naik, *Bioremediation*, **3**, 557-576 (1998).

128. A. M. Saad, H. M. Hassan and S. E. Elowa, *Afr. J. Mycol. Biotechnol.*, **8(1)**, A35-A43 (2000).

129. R. H. S. F. Vierira and V. Boya, *Int. Microbiol.*, **3(1)**, 17-24 (2000).

130. H. Runping, S. Jie, L. Jianjun, Z. Lu and B. Ggailing, *Huaxe Tongbao*, **(7)**, 25-28 (2000).

131. A. Zumariya, S. Yesim and K. Tulin, *Environ. Technol.*, **13(6)**, 579-586 (1992).

132. K. Nuray, A. Zumariya and K. Tulin, *Kim-Kim. Muhendisligi Sep.* 8^{th}, **4**, 277-282 (1992).

133. Y. Hua and R. Gerald, *J. Microbios.*, **90 (363)**, 97-109 (1997).

134. Z. Yanfu, H. Yauyan and R. Gerald, *J. Environ. Mont. Assess.*, **33(1)**, 61-70 (1994).

135. S. Kenji, *Jpn. Kokai Tokkyo Koho*, **7 pp**. (1996).

136. M. Yutaka, O. Kazuhiro, H. Fumiyasu and F. Junichiro, *Shiznoka-ken Shiznoka-kogyo Gijutsu Senta Kenteyu Hokoku*, **43**, 39-44 (1998).

137. I. Masakazu, A. Takayuki and K. Hiroichi, *Jpn. Kokai Tokkyo Koho*, **4pp**. (1998).

138. D. S. Bem, J. D. Sherman, A. Napolitano, E. A. Leon-Escamilla and G. J. Lewis, *Jpn. Kokai Tokkyo Koho*, **13pp**. (1999).

139. O. Yasushi, K. Tatsuhiro and K. Yoshinori, *Jpn. Kokai Tokkyo Koho*, **4pp**. (1999).

140. M. Ajmal, M. Ali, Y. Rehana and A. Ahmad, *Ind. J. Environ. Health*, **40(1)**, 15-26 (1998).

141. S. Gang and S. Weixing, *Ind. Engg. Chem. Res.*, **37(4)**, 1324-1328).

142. E. U. Ikhuoria and F. E. Okieimen, *Int. J. Environ. Studies,* **57(4)**, 401-409 (2000).

143. S. H. Lee, C. H. Jung, C. Hong-Suk, L. Moo-Yeal and Y. Ji-Won, Process. Biochem., 33(2), 205-211 (1998).

144. J. A. Omgbu, N. S. Ohochuku, V. Iweanya and E. M. Obaseki, *Pak. J. Sci. Ind. Res.,* 1997, **40(1-4)**, 41-43 (Pub. 1998).

145. W. T. Tan, S. T. Ooi and C. K. Lee, *Environ. Technol.*, **14**, 277 (1993).

146. C. Takahiro, K. Hiromichi, K. Toshiaki and S. Wataru, *Jpn. Kokai Tokkyo Koho*, **4pp**. (1998).

147. Z. Xin-Min and Z. Xuan, *Water Res.*, **37**, 3905-3912 (2003).

148. J. N. Min, *Avail. UMI*, **58(10)**, 5574 (B1998).

149. T. Hong Ha, T. Ba Can and L. Van Biuh, *Tap Chi Hoa Hoc*, **38(2)**, 73-76 (2000).

150. T. Tokimoto, N. Kawasaki, T. Nakamura, J. Akutagawa and S. Tanada, *J. Colloid and Interface Sci.*, **281**, 56-61 (2005).

151. J. E. Hanway, R. G. Mumford and N. P. Mishra, *AIChE Symposium series*, **75 (190)**, 306-314 (1979).

152. G. Carrillo-Moraks, M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez, A. A. Pelaaez-Cid, *J. Chromat. A.*, **938**, 237-242 (2001).

153. M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez, W. Geyer, J. Mattusch and R. Wennrich, *Colloids and Surfaces A: Physicochem. Engg. Aspects.*, **219**, 243-252 (2003).

154. G. Corro-Hermandez, M. P. Elizalde-Gonzalez and M. M. Davila-Jimenez, *J. Materials Sci.*, **38**, 1339-1346 (2003).

155. S. K. Srivastava, A. K. Singh and A. Sharma, *Environ. Technol.*, **15**, 353-361 (1994).

156. T. W. Tee and A. R. M. Khan, *Environ. Technol. Lett.*, **9**, 1223-1232 (1988).

157. D. K. Singh, B. Srivastava and R. K. Bhardwaj, *Pollut. Res.*, **20(2)**, 173-177 (2001).

158. Le Zeng, *Water Res.*, **37**, 4351-4358 (2003).

159. I. Sancedo, E. Guibal, C. H. Roulph and P. Cloirec, *Environ. Technol.*, **13**, 1101 (1992).

160. M. Abe, Y. Tanaka and M. Tsuji, *Ion Exch. Adv. Proc. IEX 92*, 326-333 (1992).

161. G. L. Rorrer, T. Y. Hsien and J. D. Way, *Ind. Chem. Engg. Res.*, **32**, 2170-2178 (1993).

162. T. Y. Hsien and G. L. Rorrer, *Sep. Sci. Technol.*, **30**, 2455 (1995).

163. K. Srinivasan, N. Balasubramanian and T. V. Ramakrishna, *Ind. J. Environ. Health*, **30(4)**, 376-387 (1988).

164. J. Yinwu, S. Zhongy and Z. Cancheng, *Faning Zhuali Shenqing Gongkai Shuomingshu*, **23 pp**. (1992).

165. E. Munah and R. Zein, *Environ. Technol.*, **18**, 359 (1997).

166. N. Khalid, P. O. Nilore, S. Ahmad, S. N. Kiam and J. Ahmad, *Sep. Sci. Technol.*, **33**, 2349 (1998).

167. N. Khalid, S. Ahmad, A. Toheed and J. Ahmad, *Adsorpt. Sci. Technol.*, **16(8)**, 655-666 (1998).

168. Q. Junqing and C. Ming, *Huanjing Gongcheng*, **17(3)**, 69-72 (1999).

169. Y. Orhan and H. Buyukgungor, *Water Sci. Technol.*, **28**, 247 (1993).

170. B. R. Reddy, N. Mirghaffari, I. Gaballah, *Resour. Conserv. Recycl.*, **21**, 227 (1997).

171. S. Al-Asheh, Z. Duvnjak, *Sep. Sci. Technol.*, **33**, 1303 (1998).

172. I. Gaballah and G. Kilbertus, *J.Geochem. Explor.*, **62**, 241 (1998).

173. M. Ayoma and M. Tsuda, *Wood Sci. Technol.*, **35**, 425-434 (2001).

174. Y. Tatsuaki, O. Akira, G. Akihiro, T. Yoshiyuki, S. Takehiko and T. Hideki, *Chiba Kogyo Daigaku Kenkyu Hoko Riko-hen*, **22**, 171-180 (1977).

175. S. Rikisaku, O. Masaru and T. Nobuhiko, *Sci. Engg. Rew. Doshisha Uni.*, **27(1)**, 41-48 (1986).

176. H. C. P. Srivastava, R. P. Mathur and I. Mehrotra, *Environ. Technol. Lett.*, **7(1)**, 55-63 (1986).

177. D. S. Bhargva, M. S. Gupta and B. S. Varshney, *Asian Environ.*, **9(41)**, 29-37 (1987).

178. S. S. Timofeeva, O. V. Lykova, G. K. Musorin and S. V. Amosova, *U. S. S. R. From: Otkrytiya, Izobret*, **(27)**, 101 (1989).

179. S. S. Timofeeva, E. E. Balad, B. F. Kukharev and V. A. Kukhareva, *U. S. S. R. From: Otkrytiya, Izobret*, **(29)**, 32 (1989).

180. B. V. Pilat, A. I. Yakumin, G. M. Paliichuk, V. N. Zaitseva and E. V. Petrukhina, *PCT Int. Appl.*, **10pp**. (1990).

181. D. K. Singh, N. K. Mishra and D. N. Saksena, *J. Inst. Engg. Chem. Engg. Div.*, **70(3)**, 90-1 (1990).

182. R. C. Vaishya and S. C. Prasad, *Ind. J. Environ. Prot.*, **11(4)**, 284-289 (1991).

183. G. Aval and I. Motedayan, *J. Chem. Engg.*, **10(2)**, 21-23 (1991).

184. S. Begum, *Sci. Inst.* (Lahore), **4(1)**, 67-68 (1992).

185. Y. S. Chung, K. W. Lee, Y. S. Yoon, S. H. Kwon and K. S. Lim, *Bull. Korean Chem. Soc.*, **13(2)**, 212-214 (1992).

186. D. K. Singh and M. K. Mishra, *Pollut. Res.*, **11(4)**, 187-190 (1993).

187. D. Andrezej and G. Woda, *I Technika Sanitarua*, **69(10)**, 344-346 (1995).

188. R. P. Singh, R. C. vaishya and S. C. Prasad, *Ind. J. Environ. Prot.*, **12(12)**, 129-138 (1995).

189. Z. A. Mahmood, *Adsorpt. Sci. Technol.*, **12(2)**, 129-138 (1995).

190. D. Suten, D. Balba and A. L. Nacu, *Celuloza si Hartie*, **45(4)**, 35-40 (1996).

191. M. Ajmal, R. A. K. Rao and B. A. Siddiqui, *Water Res.*, **30(6)**, 1478-1482 (1996).

192. C. Raji, K. P. Shukla and T. S. Anirudhan, *Ind. J. Environ. Health*, **39(3)**, 230-238 (1997).

193. C. Raji, G. N. Manju and T. S. Anirudhan, *Ind. J. Engg. Mater. Sci.*, **4(6)**, 254-260 (1997).

194. A. Masakazu, *Eco Industry*, **3(10)**, 11-17 (1998).

195. Y. S. Chung, K. W. Lee and J. Hwang, *Anal. Sci. Technol.*, **11(4)**, 254-259 (1998).

196. L. A. Voropanova and S. G. Rubanovskaya, *Khim, Prom-st.* (Moscow), **(1)**, 22-24 (1998).

197. M. Ajmal, A. H. Khan, A. Ahmad and S. Ahmad, *Water Res.*, **32(10)**, 3085-3091 (1998).

198. V. Marchetti, A. Clement, P. Gerardin and B. Loubinoux, *Wood Sci. Technol.*, **34(2)**, 167-173 (2000).

199. R. Reimert and S. Kleusch, *DGMK Tagnugsbericht*, **1**, 273-280 (2000).

200. B. Yu, Y. Zhang, A. Shukla, S. S. Shukla and K. L. Dorris, *J. Hazards. Materials*, **84(1)**, 83-94 (2001).

201. J. Marin and J. Ayele, *Environ. Technol.*, **23(10)**, 1157-1171 (2002).

202. R. Saravanane, T. Sundrarajan and R. S. Sivamurthy, *Ind. J. Environ. Health*, **44(2)**, 78-87 (2002).

203. J. Marin and J. Ayele, *Environ. Technol.*, **24(4)**, 491-502 (2003).

204. A. Meena and C. Rajagopal, *Ind. J. Chem. Technol.*, **10(1)**, 72-78 (2003).

205. T. Costodes, V. Christian, F. Henri, P. Catherine and D. Alain, *J. Hazards. Materials*, **105(1-3)**, 121-142 (2003).

206. B. Yasemin and T. Zeki, Fresenius Environ. Bull., 12(12), 1499-1504 (2003).

207. Y. S. Ho, *Fresenius Environ. Bull.*, **13(4)**, 370-373 (2004).

208. D. K. Singh and A. Mishra, *Ind. J. Environ. Health*, **32(4)**, 345-351 (1990).

209. S. V. Achari and T. S. Anirudhan, *Ind. Chem. Technol.*, **2(3)**, 137-141 (1995).

210. T. B. Geokchaev, Y. V. Efremov and R. A. Dashdiev, *Azarbaycan Neft Tasarrufati*, **(3)**, 57-61 (1989).

211. S. Ferd, *Chemische Fabrik Pott & Co.* (1925).

212. H. R. Apell, *Jpn. Kokai Tokkyo Koho*, **2pp**. (1977).

213. T. Heihachiro, *Jpn. Kokai Tokkyo Koho*, **2pp**. (1977).

214. K. Kosugi, *Jpn. Kokai Tokkyo Koho*, **2pp**. (1983).

215. E. Lassmann and M. Manfred, *Eur. Pat. Appl.* **4pp**. (1991).

216. M. Michel, C. Philippe, C. Jean-Michel and M. Gerard, *Fr. Demande*, **10pp**. (1995).

217. O. Hiroshi and A. Juji, *Jpn. Kokai Tokkyo Koho*, **4pp**. (1996).

218. Y. Masaliko and N. Sakae, *Jpn. Kokai Tokkyo Koho*, **4pp**. (1998).

219. H. M. Asfour, O. A. Fadali, M. M. Nassar and M. S. El-Geundi, *J. Chem. Technol. Biotechnol.*, **35A (1)**, 21-27 (1985).

220. A. Nag, Process. *Saf. Environ. Prot.*, **37 B_4**, 299-335 (1985).

221. M. Mazet, O. Dusart, M. Roger and D. Dussoubs-Marmier., *Revne des Sci. de I'Eau*, **3(2)**, 129-149 (1990).

222. S. R. Shukla and V. D. Sakhardande, *American Dye stuff Reporter*, **80(7)**, 38-42 (1991).

223. O. Dusart. D. Marmier-Dussoubs and B. Serpend, *Tribune de I'Eau*, **44(554)**, 15-22 (1991).

224. D. Suten, D. Balba and A. L. Nacu, *Celuloza si Hartie*, **45(4)**, 35-40 (1996).

225. N. M. Mansi, *Sep. Sci. Technol.*, **31(14)**, 1989-45 (1996).

226. N. A. Ibrahim, A. Hashem and M. H. Abou-Shosha, *Polymer-Plastic Technol. Engg.*, **36(6)**, 963-971 (1997).

227. N. A. Ibrahim, M. H. Abou-Shosha, M. Z. El-Sayed and E. El-Alfy, *Colourage Annual*, 159-164 (1998).

228. S.D. Khattri and M. K. Singh, *Water Air Soil Pollut.*, **120(3-4)**, 283-294 (2000).

229. V. Marchetti, P. Gerardin and B. Loubinoux, *Holz als Roh-und Werkstoff*, **58(1-2)**, 53-56 (2000).

230. G. Wang, Z. Song, Z. Lin and L. Wang, *J. Appl. Poly. Sci.*, **83(11)**, 2390-2396 (2002).

231. K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Venmilamani and S. Pattabhi, *Bioresour. Technol.*, **87(1)**, 129-132 (2003).

232. P. K. Malik, *Dyes and Pigments*, **56(3)**, 239-249 (2003).

233. H. Lim, S. Kim, S. M. Lee, J. Byun, S. Ryoo, Y. S. Lee and J. Yoon, *J. Indust. Engg. Chem.*, **9(4)**, 433-439 (2003).

234. A. H. Aydin, Y. Bulut and O. Yavuz, *Int. J. Environ. Pollut.*, **21(1)**, 97-104 (2004).

235. D. N. Jadhav and A. K. Vanjara, *Ind. J. Chem. Technol.*, **11 (2)**, 194-200 (2004).

236. D. N. Jadhav and A. K. Vanjara, *Ind. J. Chem. Technol.*, **11 (1)**, 42-50 (2004).

237. P. K. Malik, *J. Hazards. Materials*, **113(1-3)**, 81-88 (2004).

238. V. K. Garg, M. Amita, R. Kumar and R. Gupta, *Dyes and Pigments*, **63**, 243-250 (2004).

239. M. Ozacar and I. A. Sengil, *Process. Biochem.* (Oxford), **40(2)**, 565-572 (2005).

CHAPTER – II

SORPTION STUDIES FOR THE REMOVAL OF ZINC(II) AND CADMIUM(II) IONS ON TREATED SAWDUST OF SISSOO WOOD

INTRODUCTION

Pollution is now an important problem owing to increased industrialization and population overflow, and much effort is directed towards its control. Use of adsorbents, particularly treated sawdust, is of current interest in the removal of heavy metals from water and wastewater. In recent years the use of adsorption technique for the removal of heavy metals from wastewater has received global attention and different substances have been employed as adsorbents. Industrial wastes include heavy metals such Zn, Cd, Cu, Cr, Hg, Ni, Pb, and Mn.

Zinc is introduced into the streams by many industries [1] such as steel works with galvanizing lines, zinc and brass metal works, electroplating, viscous rayon, yarn and fiber production, ground wood pulp production and news print paper production. The zinc salts are also used in the pigment industries. Thus our aqueous environment has a high negative effect [2] due to excessive addition of zinc beyond its permissible limit (5mg/L) for aquatic life.

Cadmium is a natural, usually minor constituent of surface and groundwater. It may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids [3]. Cadmium may enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition direct discharge from industrial operations, leakage from landfalls and contaminated sites, and the dispersive use of sludge and fertilizers in agriculture. Particulate matter may rapidly adsorb much of the

cadmium entering fresh waters from industrial sources, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment [4-5].

At present, a number of technologies, such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes are used for the treatment of heavy metal-containing wastewater streams [6-8]. Thus, in industrial wastewater treatment, precipitation by means of lime, carbonates, sulphides or organosulphides has been applied.

Activated carbon has been popular choice as an adsorbent for the removal of the pollutants from wastewater [9-13] but its high cost poses an economical problem. Therefore, there is a need for the search of low cost and easily available material, which can be used more economically on large scale. Many workers have tried several cheap materials. In recent years, the use of a number of adsorbents such as moss peat [14], fly ash [15-17], red mud [18], clay [19-20], seed shell [21], Zea mays stalk [22], cactus materials [23], xanthate [24], lignin [25], chitosan [26], waste tea leaves [27], almond husk [28], and zeolites [29] has been reported for removing heavy metals from aqueous solutions. Most of these materials contain functional groups associated with proteins, polysaccharide, lignin and cellulose as major constituents, with metal uptake believed to occur through sorption processes involving such functional groups. For the removal of the toxic metals including Zn(II) and Cd(II) ions from the waste waters, it has

been reported that the agricultural by products [30] have the good capacity to adsorb the accumulated heavy metals.

Sawdust is a cheap, widely available and abundant natural material. It has been reported to exhibit ion exchange and complexation properties for the heavy metals. Singh and Mishra [31], employed iron impregnated sawdust for the removal of the phenolic compounds from water. Ajmal et al. [32] studied the adsorption of Cu(II) on sawdust. Adsorption of Cu, Pb, Hg, and Fe ions on sawdust was studied by Chung et. al.[33] and Garg et. al. [34].

This paper reports the systematic adsorption studies of Zn(II) and Cd(II) ions on treated saw dust. The effect of equilibrium time, pH, temperature and dosage of adsorbent on the adsorption of these metal ions has been described. The adsorption isotherm and probable mechanism have been explained. The removals obtained with sawdust were also compared with, results obtained with commercial activated carbon.

MATERIALS AND METHODS

ADSORBENT

The sawdust of sissoo wood (*Dalbargia sissoo*) was used in this study. It was collected from timber workshop near the University campus. It was sieved (50-60 mesh), treated with dil HCl and washed several times with distilled water. To immobilize the water-soluble substances the sawdust was treated with 2% formaldehyde in the ratio of 1:3 (sawdust: formaldehyde, w/v) at 50^0C for 6 hours. The sawdust was filtered and washed with distilled water to remove free formaldehyde. It was then used throughout the adsorption studies.

ADSORBATE SOLUTION

The stock solution (1000 mg/L) of metal ions was prepared by dissolving their corresponding nitrate salts in double distilled water. The solution was further diluted to the required concentrations before use. All the chemicals used were analytical reagent grade and were obtained from Loba, E. Merk and BDH Mumbai (India).

BATCH ADSORPTION STUDIES

Adsorption studies were carried out at different temperatures (25-60° C). 50 ml of the solution containing the desired quantity of the metal ion was treated with 0.5 g of treated sawdust in stoppered conical flasks for the different times using a temperature-controlled shaker. After the predetermined time interval the reaction mixture was filtered and the filtrate was analyzed for the final concentration of the

metal ions by atomic absorption spectrometry. The amount of adsorbed metal ions was calculated from the difference of initial and final concentration of metal ions. Blanks were also prepared to find out the adsorption onto the internal surface of the containers, if any. The effect of pH of the solution was adjusted by either 1.0 N HCl or NaOH solution. The adsorption of Zn(II) and Cd(II) from aqueous solutions by powdered activated carbon (0.150-0.038 mm) (Merck) was studied to compare the adsorption effectiveness of treated sawdust. The adsorption experiments were also conducted to determine the equilibrium time, the optimum pH and the dosage of the adsorbent for the maximum adsorption.

ADSORPTION MODEL

To quantify, the adsorption capacity of treated sawdust for the removal of metal ions from water solutions, the Langmuir and Freundlich equations were applied.

(a) Langmuir Model- According to this model-

$$Ce/Am = 1/k\ 1/b + (1/b)\ Ce \qquad (1)$$

where 'Ce' is the equilibrium concentration (mole/L), 'Am' is the amount adsorbed per specified amount of adsorbent (m. moles/g), 'k' is the equilibrium constant and 'b' is the amount of adsorbate required to form monolayer. This model deals with the monolayer adsorption of adsorbate on the adsorbent.

(b) Freundlich Model- According to this model-

$$Am = kCe^{1/n} \text{ or } \ln (Am) = \ln k + 1/n\ [\ln(Ce)] \qquad (2)$$

where all the terms have the usual significance and 'n' is an empirical constant. This model deals with the multilayer adsorption of the substance on the adsorbate. The points in the figures indicate the observed data and the line corresponds to the fitted data.

The thermodynamics, parameters ΔG, ΔH and ΔS were computed from the equation given below and listed in table. The free energy change was calculated from the relations.

$$\Delta G = - RT \ln k \qquad (3)$$

Similarly, the enthalpy change ΔH between 25 to 60° C was computed from the following equations.

$$\ln k = -\Delta H/RT + C \qquad (4)$$

and the entropy change was calculated from the equation

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

RESULTS AND DISCUSSION

TIME OF EQUILIBRIUM

The adsorption of Zn(II) and Cd(II)ions was studied with time and results are shown in Figure 2.1. The adsorption increases with increasing contact time and the equilibrium was attained after shaking for 80 minutes. It is observed that the adsorption of Zn(II) ions reaches to a final plateau after 70 minutes. The maximum uptake after this time is constant at a value of 75% adsorption. On the other hand, the behaviour of Cd(II)ions reaches to a value of 72%. However, the time of equilibrium used in all the following studies was set to 1.5 hour for the sake of simplicity as well as to ensure the complete process of adsorption in both cases.

EFFECT OF DOSE OF SAW DUST

The effect of the dose of treated sawdust on the adsorption of Zn(II) and Cd(II)ions has been presented in Figure 2.2. The percent adsorption increases with increase in the dose of adsorbent probably due to its high surface area. But the adsorption increases in a steeped fashion. In case of Zn(II) ions, the final plateau is attained at 60% adsorption for a dose of > 16 g of treated saw dust per 1000 ml of metal ion solution. On the other hand Cd(II) ions show two steps adsorption process which is initially very fast compared to Zn(II) ions and reaches to final plateau equivalent to 68% adsorption. This plateau was adsorbed at dose of > 16 g of treated sawdust per 1000 ml of solution.

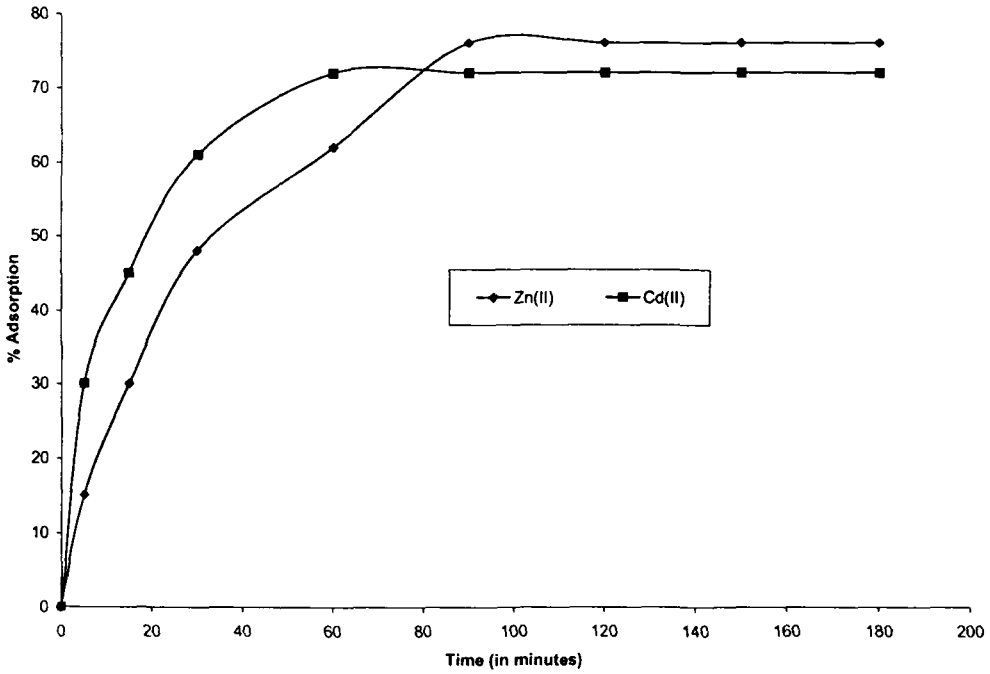


Figure 2.1. Effect of time for the adsorption of Zn(II) and Cd(II) ions on treated sawdust.

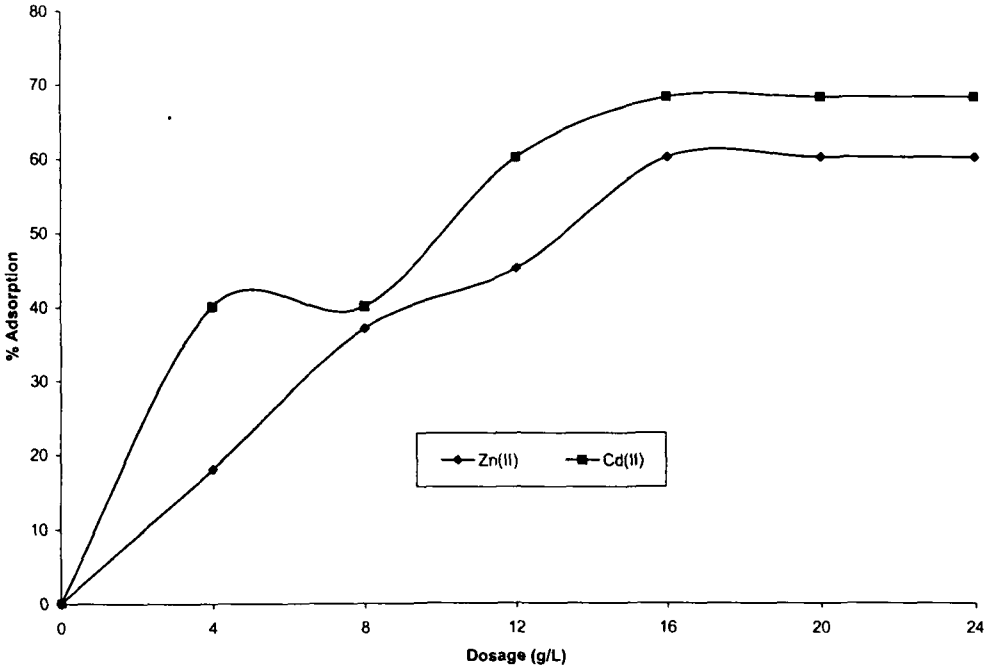


Figure 2.2. Effect of dosage of treated sawdust on the adsorption of Zn(II) and Cd(II) ions.

EFFECT OF pH

The percent adsorption for Zn(II) and Cd(II) ions increased with increasing pH and reached plateau at pH 10-12 for Zn(II) ions and pH 6-12 for Cd(II) ions as shown in Figure 2.3. The pH of the aqueous solution is an important controlling parameter in the adsorption process [35] and thus the role of hydrogen ion concentration was examined from solutions at different pH covering a range of 2-12. Both the metal ions show different extent of adsorption at different pH values of treated sawdust. The adsorption of Zn(II)ions starts only after pH 6. About 36% adsorption of Zn(II)ions is observed around pH 8, which reaches to a maximum value of 70% at pH 10 and remains constant thereafter. On the other hand the adsorption of Cd(II) ions starts at pH 2. It reaches up to 30% at pH 4, 60% at pH 6 and finally to a maximum value of 62% adsorption at pH 6.7 and remains constant at this level even at higher pH values.

The adsorption behaviour of Zn(II) and Cd(II) ions on sawdust at different pH values may be explained through the ion exchange and complexation mechanisms.

Sawdust basically contains lignin and cellulose. The polar functional groups of lignin e.g., aldehydes, ketones, alcohols, acids and phenolic hydroxides are involved in these processes. They are affected by pH and may undergo protonation and/or deprotonaiton resulting thereby the variation in surface charge of the adsorbent [36]. This results the uptake of the metal ions from the solution via complexation and/or ions exchange processes. These ions show similar trends of

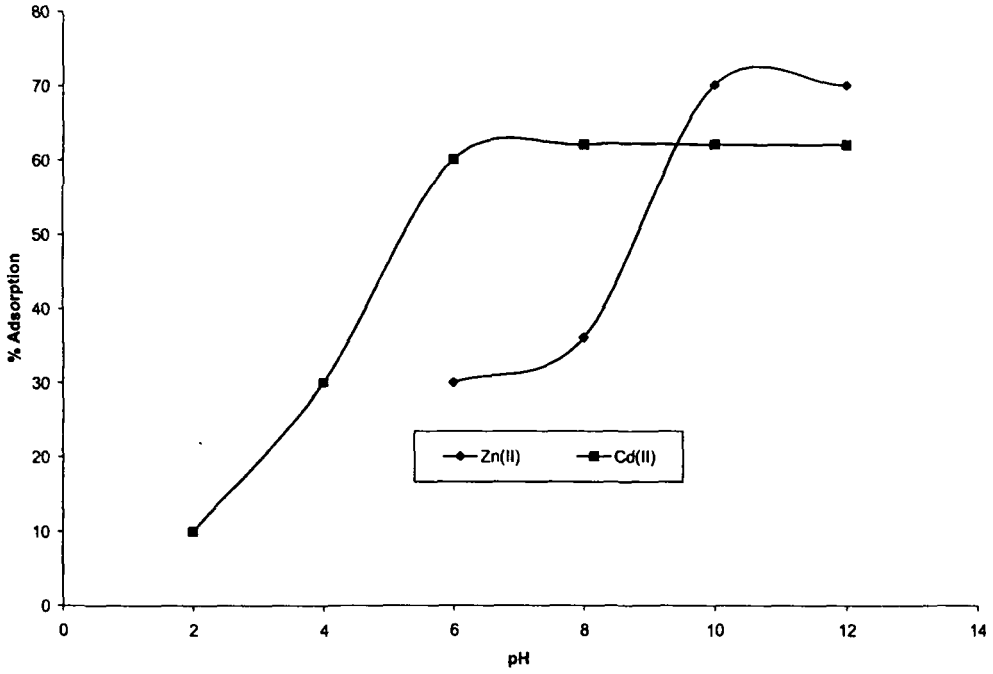


Figure 2.3. Effect of pH on the adsorption of Zn(II) and Cd(II) ions on treated sawdust.

adsorption probably because they belong to the same group of the periodic table. Their different extents of adsorption may be attributed to their different effective ionic radii. The ionic radius of Cd(II) ions is 5 A° while that of Zn(II) ions is 6 A°. The smaller ionic size of Cd(II) ions helps in its easy approach to the less approachable sites of the adsorbent as compared to that of Zn(II) ions. Further the more hydration energy of Cd(II) ions in comparison of Zn(II) ions restricts its maximum uptake by the adsorbent.

ADSORPTION ISOTHERM STUDIES

The adsorption isotherms of Zn(II) and Cd(II) ions on treated sawdust are shown in Figures 2.4(a) and 2.4(b). From the adsorption curves, we presumed that the adsorption followed Langmuir adsorption isotherm. From equation (1), a plot of Ce/Am versus Ce should be a straight line with a slope 1/b and intercept as 1/kb. Langmuir adsorption isother of Zn(II) and Cd(II) ions at different temperature are presented in Figures 2.5(a) and 2.5(b). It is evident from this figure that the adsorption of Zn(II) and Cd(II) ions from aqueous solution on to the treated sawdust fits well the Langmuir adsorption isotherm because of high correlation coefficient value (R=0.99). The values of k and b were calculated from the slope and intercept of the plots of Ce/Am versus Ce. The constant values obtained from Langmuir isotherm are listed in Table 2.1 and Table 2.2. The multilayer adsorption process is not possible in case of Langmuir model. It is only possible in

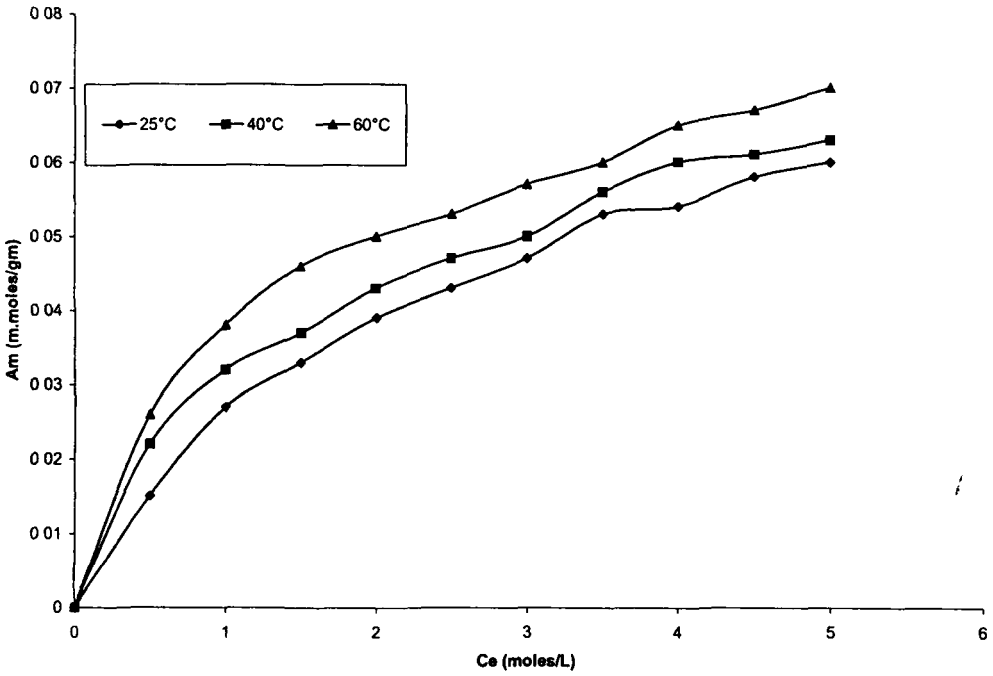


Figure 2.4(a). Adsorption isotherm of Zn(II) ion on treated sawdust at different temperatures.

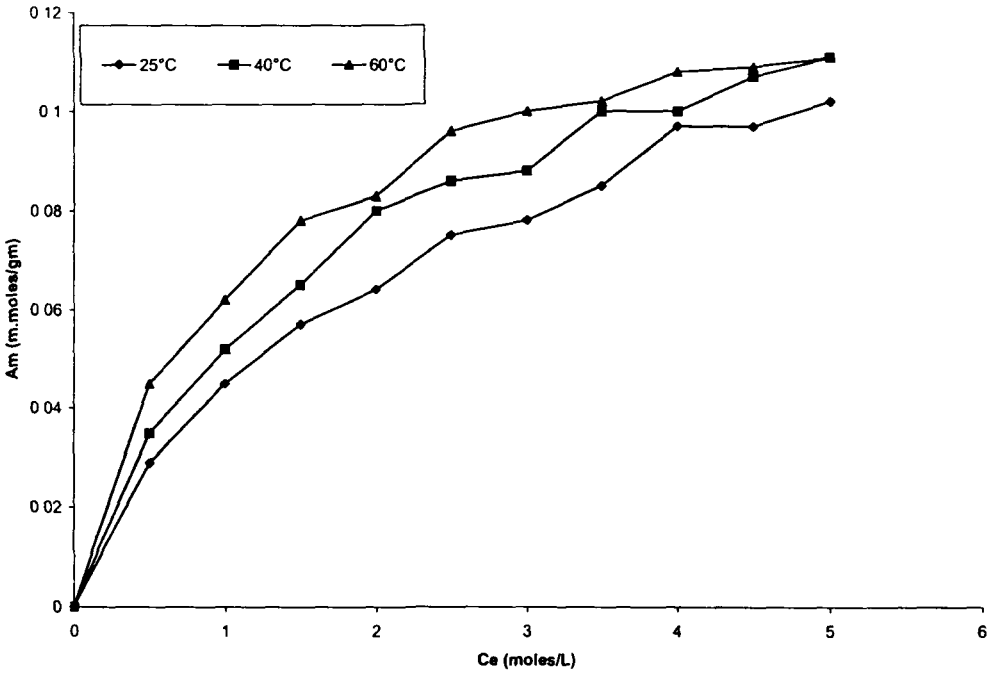


Figure2.4(b). Adsorption isotherm of Cd(II) ion on treated sawdust at different temperatures.

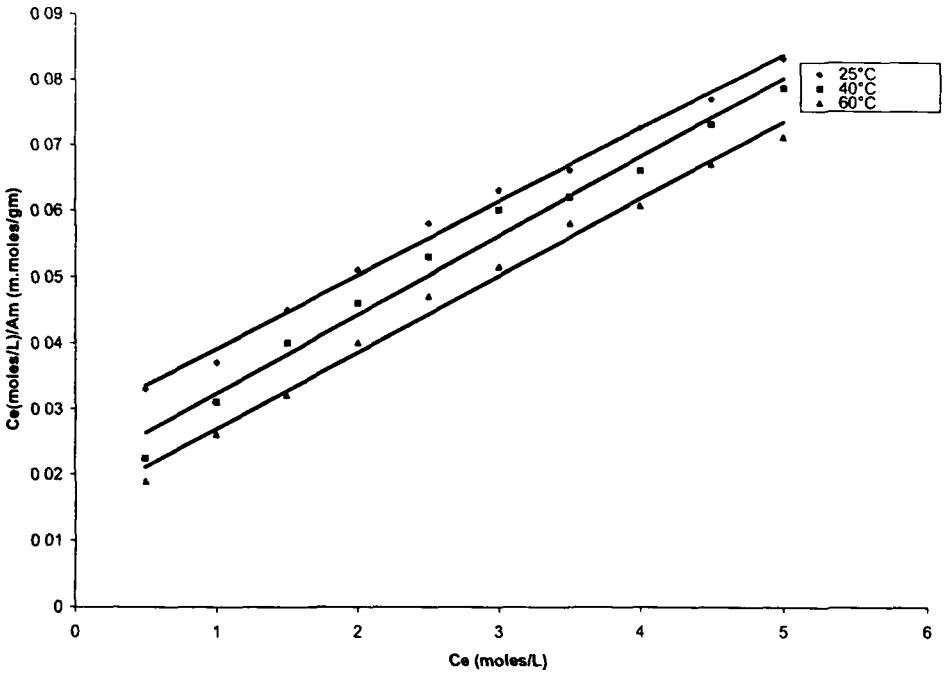


Figure 2.5(a). Langmuir adsorption plot for the adsorption of Zn(II) ion by treated sawdust.

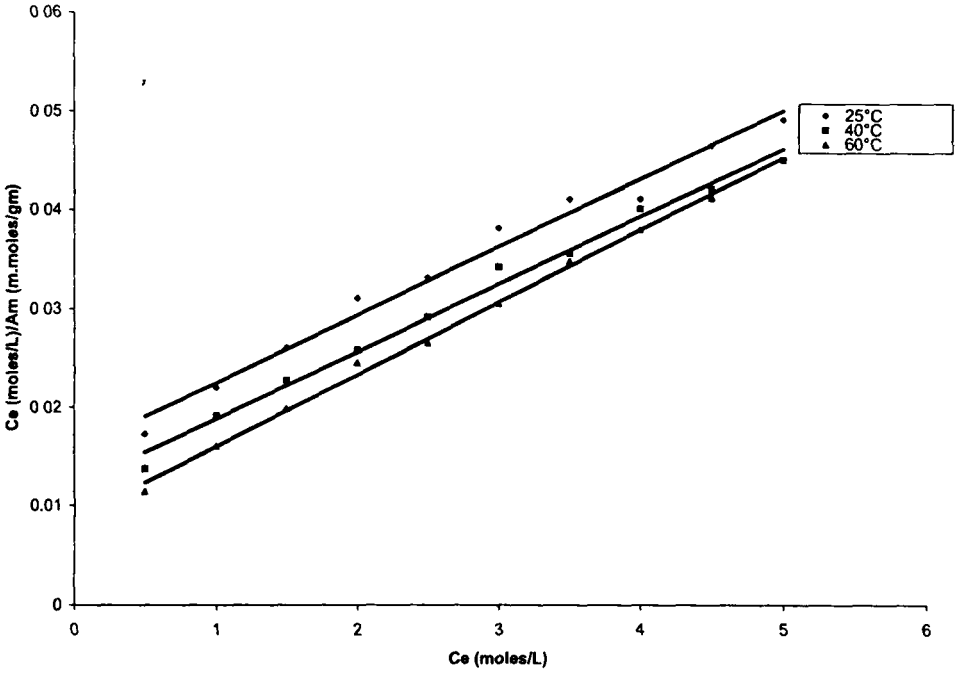


Figure2.5(b). Langmuir adsorption plot for the adsorption of Cd(II) ion by treated sawdust.

TABLE-2.1

Langmuir parameters for the adsorption of Zn(II) ion on treated sawdust at different temperatures

Temp.	Reg. Coeff.	Langmuir Constants	
(^{0}C)	(R)	K	b
25	0.996	0.396	90.09
40	0.991	0.583	84.03
60	0.994	0.758	86.20

TABLE-2.2

Langmuir parameters for the adsorption of Cd(II) ion on treated sawdust at different temperatures

Temp.	Reg. Coeff.	Langmuir Constants	
(^{0}C)	(R)	K	b
25	0.991	0.442	144.93
40	0.995	0.571	147.05
60	0.998	0.848	136.98

Freundlich adsorption model where the surface of the sawdust is assumed to be made up of heterogeneous patches, which are homogenous in themselves.

Initially the adsorption of Cd(II) ions at all the temperature occurs in the unhydrated form, i.e., the dehydration of both the ions and the adsorption site occurs first and the ions get adsorbed on the most easily accessible surface sites (exposed sites). However the sites at the inner surface are still available. On increasing the concentrations of the ions in the solution, the aggregation of these ions increases on the surface leading to their access to the less accessible sites (i.e. the inner surface sites). This tends to an increase in the adsorption through the opening of the pores of adsorbent due to its swelling. The later effect facilitates the entry of water molecules too into the pores. On the entry of water, the adsorbed ions/sites get hydrates leading to a decrease/reversal in the extent of adsorption.

Based on Langmuir isotherms, the increase of percent adsorption implied that more active sites were probably at high temperature. Heat of adsorption (ΔH), which indicates the mechanism of adsorption, was calculated by van't Hoff equation [Eq. (4)], where R is the universal gas constant (8.31 J/mol K), and T is the absolute temperature (K).

A plot of ln k versus 1/T yields a straight line as shown in Figures 2.6(a) and 2.6(b). The ΔH value was found to be 17.706 kJ/mole for Zn(II) ions and 16.999 kJ/mole for Cd(II) ions which indicated the endothermic reaction.

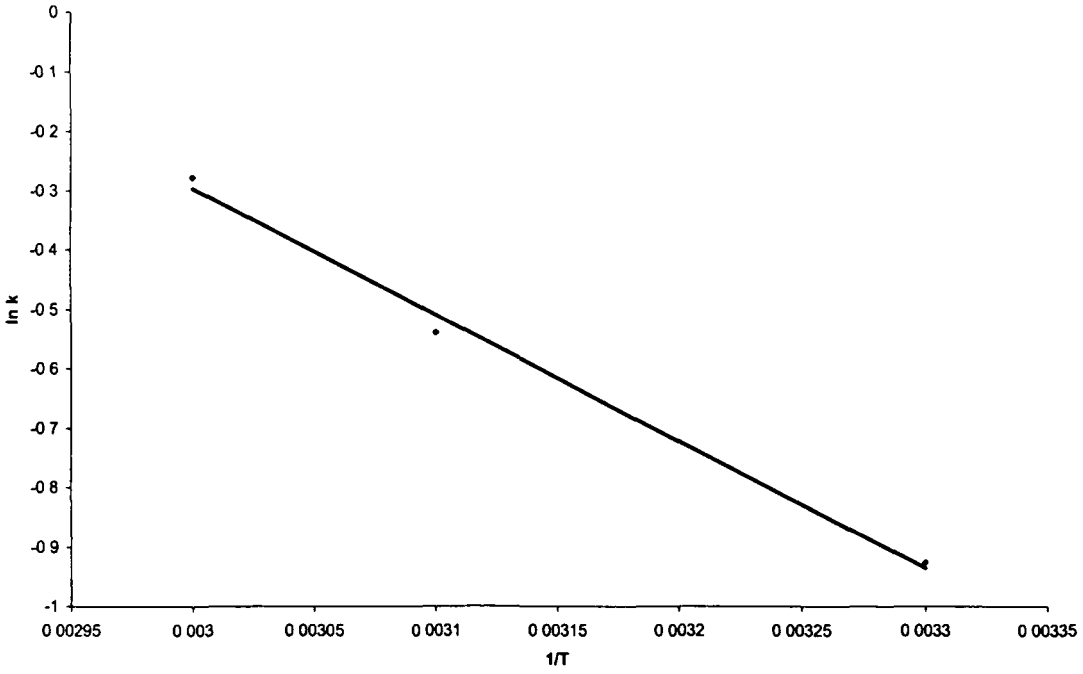


Figure 2.6(a). Plot of Langmuir constant (ln k) against temperature (1/T) for Zn(II) ion.

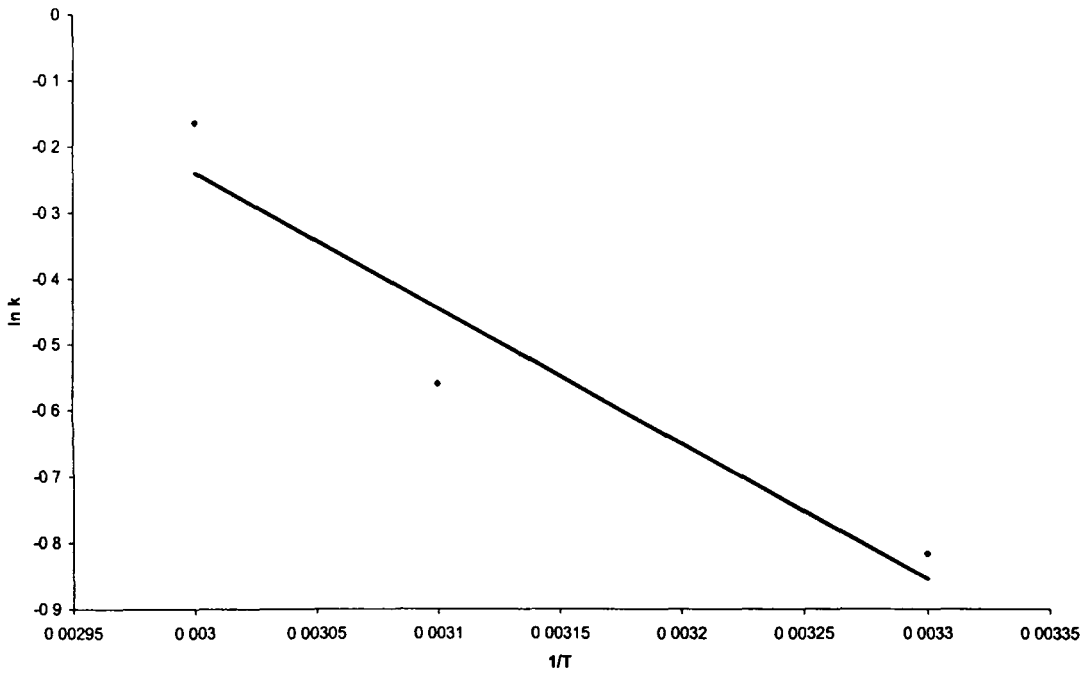


Figure 2.6(b). Plot of Langmuir constant (ln k) against temperature (1/T) for Cd(II) ion.

THERMODYNAMIC PARAMETER OF SORPTION

The various thermodynamic parameters, i.e., free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), associated with the sorption of Zn(II) and Cd(II) ions on to the treated sawdust were determined by using the equations (3), (4), and (5) and the values are listed in Table 2.3 and Table 2.4, where R is the universal gas constant (8.31 J/mole K), k is the equilibrium constant and T is the absolute temperature (K) [37,38].

It is clear from the tables that the positive values of ΔH show the sorption to be of endothermic in nature. Moreover, the positive values of ΔS point out some structural changes as a result of the interaction of Zn(II) and Cd(II) ions with the active sites of treated sawdust.

COMPARATIVE STUDY OF ADSORPTION PROPERTIES OF ACTIVATED CARBON AND TREATED SAWDUST FOR Zn(II) AND Cd(II) IONS

Since sawdust was considered as a cheap alternative to more costly materials, activated carbon, a common adsorbent, was investigated for the removal of Zn(II) and Cd(II) ions. Activated carbon was found to have a much higher adsorption capacity for Zn(II) and Cd(II), especially at low dosages, on the other hand, sawdust proved to be as effective as activated carbon at high dosages (Figure 2.7(a) and 2.7(b)). The specific area of the sawdust is 677 m^2/g versus 400-2000

TABLE –2.3

Thermodynamic parameters for the adsorption of Zn(II) ion on treated sawdust at different temperatures

Temp.	Langmuir Adsorption Isotherm			
(^{0}C)	ln k	ΔG	ΔS	ΔH
25	-0.926	2.293	0.0517	17.706
40	-0.539	1.401	0.0520	
60	-0.277	0.766	0.0508	

ΔG = kJmole^{-1}, ΔS = kJmole^{-1}K^{-1}, and ΔH = kJmole^{-1}

TABLE –2.4

Thermodynamic parameters for the adsorption of Cd(II) ion on treated sawdust at different temperatures

Temp.	Langmuir Adsorption Isotherm			
(^{0}C)	ln k	ΔG	ΔS	ΔH
25	-0.816	2.020	0.050	16.949
40	-0.560	1.456	0.049	
60	-0.164	0.453	0.049	

ΔG = kJmole^{-1}, ΔS = kJmole^{-1}K^{-1}, and ΔH = kJmole^{-1}

m^2/g of commercial activated carbon. Although sawdust has relatively low metal adsorption capacity, it can be obtained cheaply in large quantities. Moreover, it has acid neutralizing capacity, which can be attractive for use in acidic industrial wastewater treatment process. Similar results have been previously reported for Zn(II) and Cd(II) adsorption onto activated carbon and sawdust [39-41].

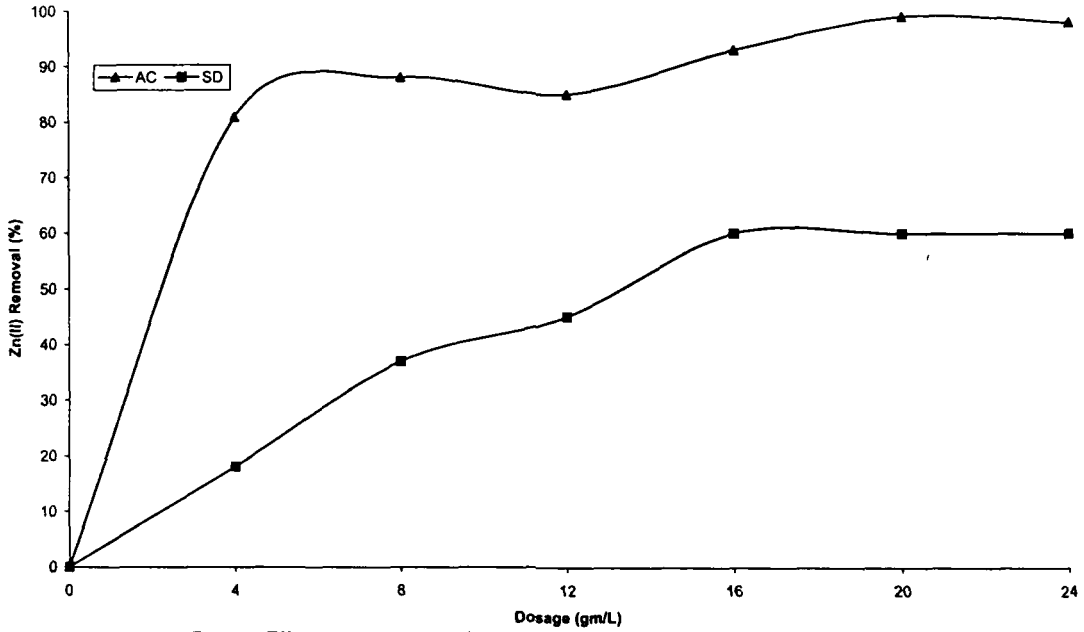


FIGURE 2.7(a). Effectiveness of an activated carbon(AC)-compared to Sawdust(SD)- on the removal of Zn(II) ion.

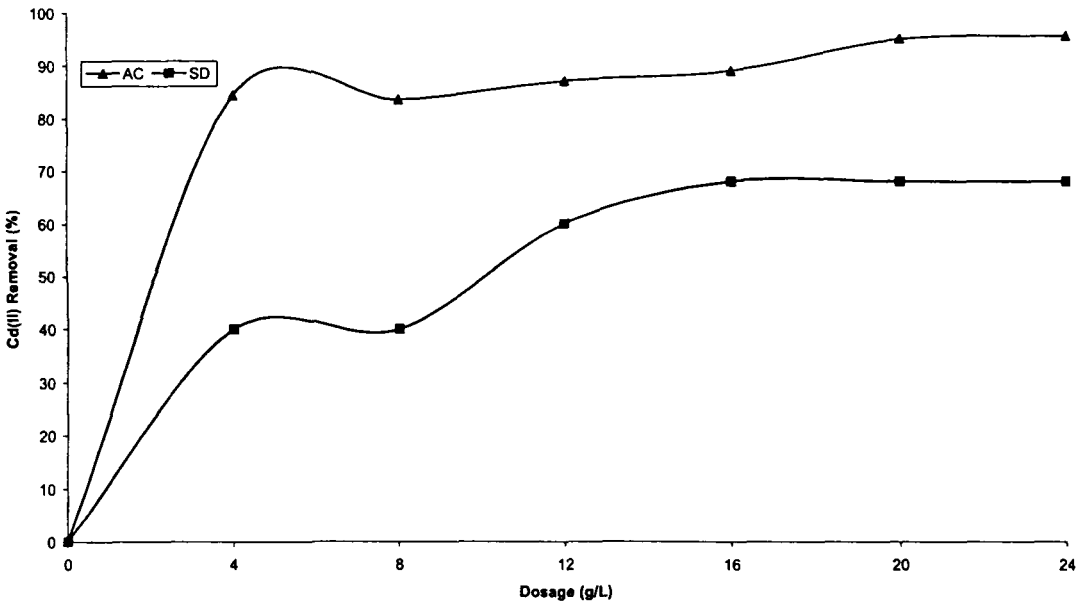


FIGURE 2.7(b). Effectiveness of an activated carbon(AC)- compared to Sawdust(SD)- on the removal of Cd(II) ion.

REFERENCES

1. R. L. Ramos, L. A. B. Jacome, J. M. Barron, L. F. Rubio and R. M. G. Cornado, *J. Hazard. Mater.*, **90**, 27-38 (2002).
2. L. Moser and N. Adhaum, *Sep. Purif. Technol.*, **26**, 137 (2002).
3. Organisation for Economic Co-operation and Development (OECD), *Risk Reduction Monograph No. 5: Cadmium OECD Environment Directorate, Paris, France*, (1994).
4. World Health Organisation (WHO). *Environmental Health Criteria 134 - Cadmium International Programme on Chemical Safety (IPCS) Monograph,* (1992).
5. V. Forstner and W. Wittman, *Metal pollution in the aqutic environment. Springer-Verlag, Berlin/Heidelberg/New York*, p. 12, (1981).
6. P. Kaewsarn and Q. Yu, *Separation Sci. Technol.*, **34**, 1595-1605 (1999).
7. M. Suzuki, *Water Sci Technol.*, **35**, 01-11 (1997).
8. K. Chandra Sekhar, S. Subramanian, J. M. Modak and K. A. Natarajan, *Int. J. Miner. Process.*, **53**, 107-120 (1998).
9. M. Chan-Jun, L. Jung-heon, *Process Biochemistry (Oxford, United Kingdom)*, **40(3-4)**, 1279-1283 (2004).
10. K. Santhy, and P. Selvapathy, *Separation Sci. Technol.*, 39**(14)**, 3331-3351 (2004).

11. R. R. Bansode, J. N. Losso, W. E. Marshall, R. M. Rao and R. J. Portier, *Bioresource Technol.*, **89(2)**, 115-119 (2003).

12. K. V. Kumar and K. Subanandam, *Chemical Industry Digest*, **16(1)**, 55-58 (2003).

13. R. Saravanane, T. Sundararajan and S. S. Reddy, *Ind. J. Environ. Health,* **44(2)**, 78-87 (2002).

14. B. L. Summers, L. B. Gress, W. H. Philipp and S. B. Eastep, *Peat-moss pellets for removal of metal-ion contaminants dissolved in dilute wastewater U.S.*, 11 pp., Cont.-in-part of U.S. Ser. No. 249, 733.

15. F. Ferrero, P. Gaglia and P. Maria, *Annali di Chimica (Rome)*, **86**, 125-132 (1996).

16. A. Mathur, S. K. Khare and D. C. Rupainwar, *J. Indust. Pollut. Control,* **5**, 52-57 (1989).

17. B. Bayat, *Water Air and soil Pollution,* **136**, 69-92 (2002).

18. R. Apek, E. Tuten, M. Hugul and M. Hizal, *Water Res.*, **32**, 430-440 (1998).

19. B. J. W. Tuin and M. Tels, *Environ. Technol.*, **11**, 1039-1052 (1990).

20. D. V. Ladonin, *Pochvovedenie*, **(10)**, 1197-1206 (2003).

21. M. Ajmal, M. Ali, Y. Rehana and A. Anees, *Ind. J. Environ. Health,* **40(1)**, 15-26 (1998).

22. E. U. Ikhuoria and F. E. Okieimen, *Int. J. Environ. Studies,* **57(4)**, 401-409 *(2000).*

23. M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez, W. Geyer, J. Mattusch and R. Wennrich, *Colloid and Surfaces A: Physicochem. Eng. Aspects*, **219**, 243-252 (2003).

24. J. E. Hanway, R. G. Mumford and P. N. Mishra, *AICHE Symposium Series*, **75**, 306-314 (1979).

25. S. K. Srivastava, A. K. Singh and A. Sharma, *Environ. Technol.*, **15**, 353-361 (1994).

26. G. L. Rorrer, T. Y. Hsien and J. D. Way, *Ind. Chem. Engg. Res.*, **32**, 2170-2178 (1993).

27. T. W. Tee and A. R. M. Khan, *Environ. Technol. Lett.*, **9**, 1223-1232 (1988).

28. H. Hasar, Y. Cuci, E. Obek and M. F. Dilekoglu, *Adsorp. Sci. Technol.*, **21**, 799-808 (2003).

29. S. K. Ouki and M. Kavannagh, *Water Sci. Technol.*, **39**, 115-122 (1999).

30. D. Mohan and K. P. Singh, *Water Res.*, **36**, 2304-2318 (2002).

31. D. K. Singh and A. Mishra, *Ind. J. Environ. Health,* **32**, 345-351 (1990).

32. M. Ajmal, A. H. Khan, S. Ahmad and A. Ahmad, *Water Res.*, **32**, 3085-3091 (1998).

33. Y. S. Chung, K. W. Lee, Y. S. Yoon, S. H. Kwon and K. S. Lim, *Bull. Korean Chem. Soc.*, **13**, 212-214 (1992).

34. V. K. Garg, R. Gupta, A. B. Yadav and R. Kumar, *Bioresour. Techonol.*, **89**, 121-4 (2003).

35. H. A. Elliot and C. P. Huang, *Water Res.*, **15(7)**, 849-855 (1981).

36. C. P. Huang and E. A. Rhoads, *J. Colloid Interface Sci.*, **131(2)**, 289-306 (1989).

37. B. Acemioglu and M. H. Alma, *Holz als Roh- und Werkstoff.*, **62(4)**, 268-272 (2004).

38. M. Ajmal, A. H. Khan, S. Ahmad and A. Ahmad, *Water Res.*, **32(10)**, 3085-3091 (1998).

39. C. P. Huang and M. O. Corapcioglu, *Water Res.*, **21(9)**, 1031-1044 (1987).

40. B. E. Reed and M. R. Matsumoto, *Separation Sci. Technol.*, **28(13-14)**, 2179-2195 (1993).

41. P. Marzal, A. Seco and C. Gabaldon, *J. Chem. Tech. Biotechnol.*, **66**, 279-285 (1996).

CHAPTER – III

ADSORPTION DYNAMICS AND EQUILIBRIUM STUDIES OF HEAVY METAL IONS ONTO MANGO SAWDUST

INTRODUCTION

The presence of toxic heavy metals in industrial effluents has become a matter of environmental concern. Mining, tannery, jewelry, chemical, metallurgical, electrical and electronics large scale industries in industrial nations, and also arts and crafts in developing countries [1] are the main source for metal containing waste pollution. The effect of waste as sludge deposition and wastewater on flora, on marine life and on public health has invited numerous research activities. Increasingly strict discharge limits on heavy metals and their widespread uses, threatening presence at hazardous waste sites have accelerated the search for advanced and economically attractive treatment technologies for their removal. Heavy metals removal from aqueous solution has been commonly carried out by several process, chemical precipitation, solvent extraction, ion exchange, reverse osmosis or adsorption [2-3]. Chemical precipitation, in particular, this is the most prevalent method but not suitable for removing low concentration of heavy metal ions. Adsorption processes are promising in this regard as opposed to more conventional chemical precipitation in that way achieve higher level removals over a wider range of solution conditions. The adsorption, with the selection of suitable adsorbents, can be an effective technique for the removal of heavy metals from wastewater [4]. Some of the suggested adsorbents are moss peat [5], fly ash [6-7], activated carbon [8-10], zeolite [11], chitosan [12], lignin [13], clay [14], biomass [15-16], xanthate [17] and cactus material [18]. All the adsorbents are not

economically suitable enough for waste water treatment. Though they generally have high metal adsorption capacity but are expensive and difficult to be separated from the wastewater after use. Therefore, now a days, a growing research interest has been developed in search of low cost alternatives to these adsorbents. Sawdust has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to its abundance, easy availability and low cost. Further it will be a step ahead toward exploring the possibility of the use of waste biomass for industrial wastewater pollution management. The studies on the use of mango sawdust as adsorbent are limited. It is a common tree present all over India. Timber of mango tree is widely used for furniture making and the waste sawdust so produced is generally used as cooking fuel due to its negligible cost.

The aim of the present study was to determine the optimum condition for the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) from aqueous solutions. The effect of retention time, temperatures, concentration and dose on the adsorption of heavy metals by mango sawdust has been studied. The adsorption isotherms and the probable mechanism have been explained.

MATERIALS AND METHODS

ADSORBENT

The sawdust of Mango tree (*Mangefera indica*) was used as an adsorbent for the removal of Cu(II), Cr(III), Ni(II) and Pb(II) from aqueous solutions. It was collected from timber workshop near the University campus. Sawdust was washed with hot distilled water to clean the adhering dirt. It was sieved in the size range 50-60 mesh and treated with dilute HCl and washed several times with distilled water until no chloride was released and activated at 100°-105°C for 24h. It was then used throughout the adsorption studies.

ADSORBATE SOLUTIONS

The stock solution (1000 mg/L) of metal ions was prepared by dissolving their corresponding nitrate salts in double distilled water. The solution was further diluted to the required concentrations before use. All the chemicals used were of analytical reagent grade and were obtained from Loba, E. Merk and BDH Mumbai (India).

ADSORPTION EXPERIMENTS

The studies of the kinetics of adsorption were carried out at room temperature (27±2°C). 100 ml of the solution containing the desired quantity of the metal ion was treated with 5.0 gm of sawdust in stoppard conical flasks for the different times using a temperature-controlled shaker. The solution-sawdust mixtures were stirred at 100

rpm and at the end of predetermined time interval the reaction mixture was filtered and the filtrate were analyzed for its metal ions contents.

The batch equilibrium studies for the determination of the effect of optimum metal ion concentration were conducted for the equilibrium time mixing at a constant speed of 100 rpm to obtain valve of maximum adsorption.

Batch adsorption experiments at various sawdust dosages (2.0-10.0 gm) in 100 ml of solution were also studied with the equilibrium time mixing at 100 rpm for maximum adsorption at room temperature. The concentration of metal ions in the supernatant was measured using atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

ADSORPTION EQUILIBRIUM TIME

Preliminary kinetic experiments were conducted to asses the time taken for the equilibrium to be obtained and the results are presented in Figure 3.1 for different metal ions. It is readily apparent from the figure that significant removals of different metal ions occurred in 20 minutes and no appreciable changes in terms of removal were noticed after 120 minutes. In all subsequent experiments the equilibrium time was maintained at 120 minutes, which was considered as sufficient for the removals of different metal ions by mango sawdust.

EFFECT OF INITIAL METAL CONCENTRATION

The effect of changing the initial concentration of the adsorbate on adsorption, while keeping the dosage of the sawdust constant (5.0 gm in 100 ml of solution) at room temperature, was studied. The increase of the initial concentration of Cu(II), Cr(III), Ni(II) and Pb(II) from 100 to 600 mgL^{-1}, the percentage adsorption increases from 78-90 for Cu(II), 80-91 for Cr(III), 85-97 for Ni(II) and 90-96 for Pb(II) see Figure 3.2. As a result of the above observations, it was indicated that the adsorption process of different heavy metal ions on sawdust was to be dependent on concentration of solute up to some extent.

EFFECT OF DOSAGE ON ADSORPTION PROCESS

The effect of sawdust dose on the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) is presented in Figure 3.3. The amounts of sawdust that is added to the solutions

keeping the metal ions concentration constant (100 mgL^{-1}). It was observed that the adsorption increases with the increase in the dose of sawdust. The adsorption of Cu(II) by sawdust increases from 65-89%, Cr(III) increases from 68-94%, Ni(II) increases from 73-97% and Pb(II) increases from 76-96% respectively, by increasing the sawdust dosage from 2.0 to 10.0 gmL^{-1} under equilibrium conditions. The maximum uptake is exhibited at 10.0 gm of adsorbent.

EFFECT OF TEMPERATURES ON ADSORPTION PROCESS

Adsorption studies were performed at four temperatures namely, 10, 20, 30 and 40°C. The effect of temperature variation on the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) from aqueous solution is presented in Figure 3.4. From this figure it is clear that the adsorption increases along with an increase of temperature.

ADSORPTION DYNAMICS

The two important aspects for parameter evaluation of the adsorption study are the kinetic and the equilibrium of adsorption. The models of adsorption kinetics correlate the solute uptake rate, in water treatment process design. In this study, for a batch reaction, conducting the adsorption of heavy metals on adsorbent followed the adsorption dynamics.

First-order reversible reaction model

The adsorption of heavy metals from liquid phase to solid phase can be considered as a reversible reaction with an equilibrium being established between two phases

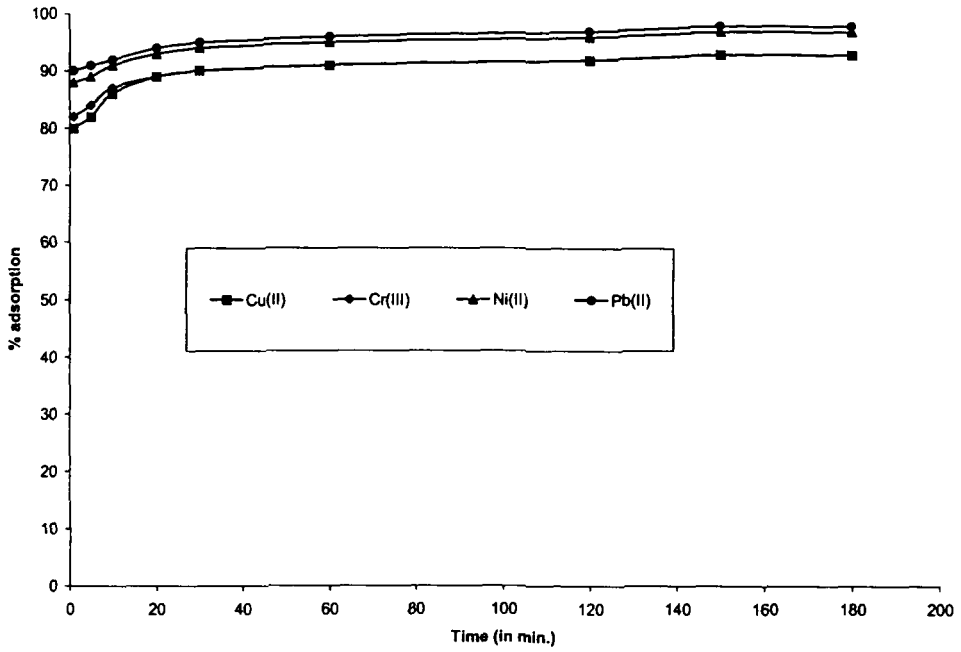


Figure 3.1. Equilibrium time for the adsorption of different metal ions.

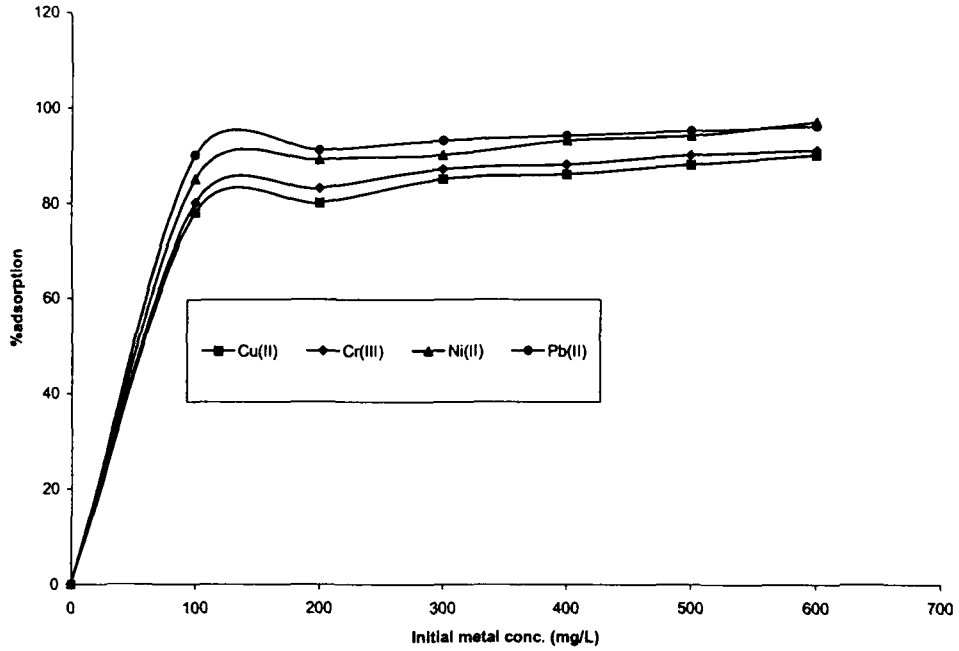


Figure 3.2. Effect of initial metal concentration on the adsorption of different metal ions.

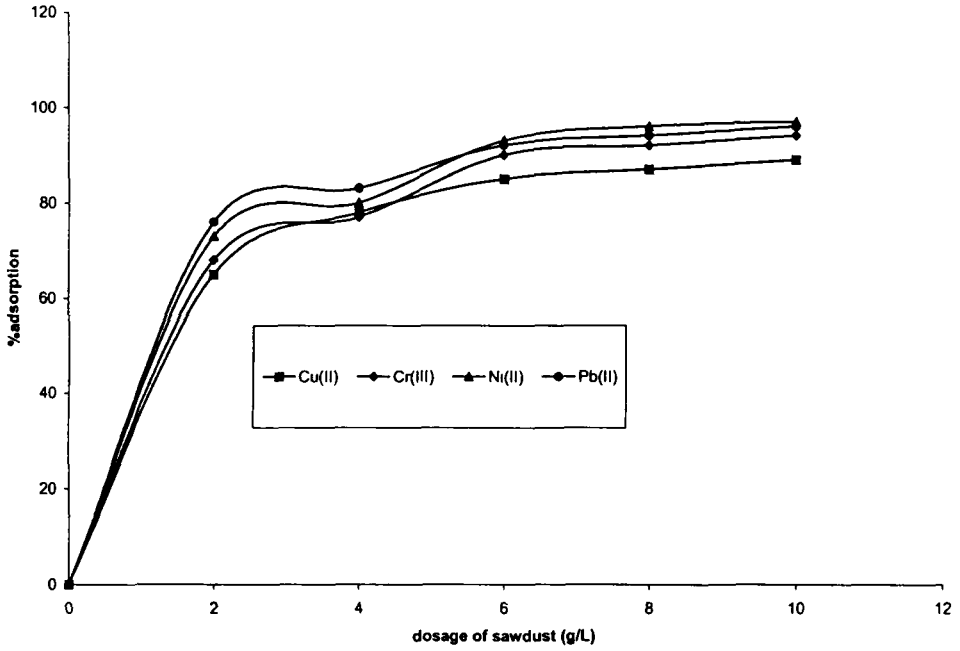


Figure 3.3. Effect of sawdust dosage on the adsorption of different metal ions.

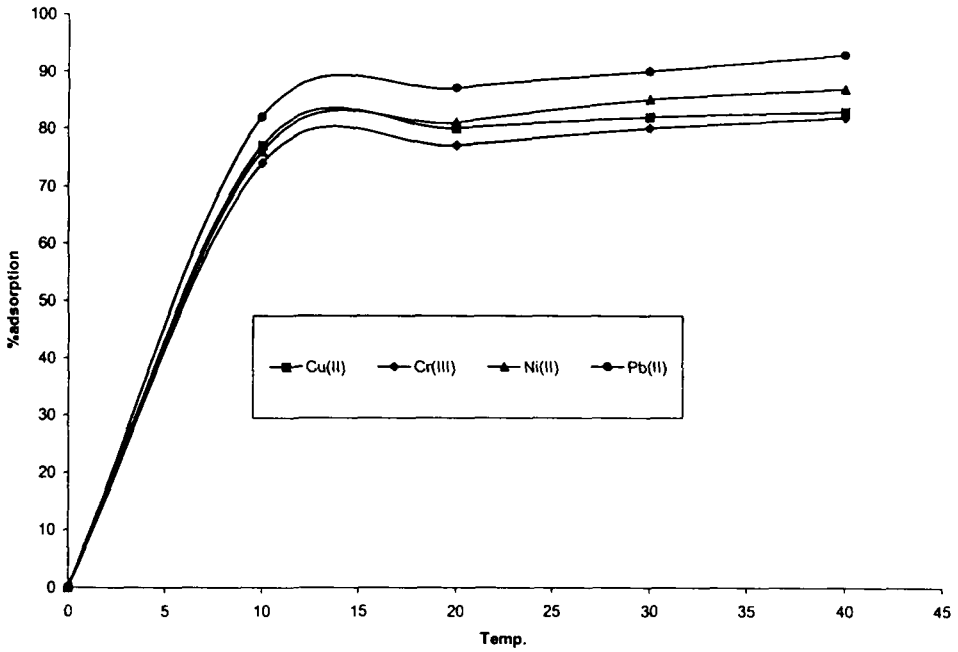


Figure 3.4. Effect of temparature on the adsorption of different metal ions.

[19]. A simple first-order reaction model was, therefore, used to correlate the rates of reaction, which can be expressed as,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad (1)$$

If this model holds true, the rate equation for the reaction is expressed as,

$$dC_B/dt = dC_A/dt = k_1C_A \; k_2C_B = C_{Ao}\,(dX_A/dt)$$

$$= k_1\,(C_{Ao} \; C_{Ao}\,X_A) \; k_2\,(C_{Bo} \; C_{Ao}\,X_A) \qquad (2)$$

where C_B (mg/g) is the concentration of heavy metals on the adsorbent and C_A (mg/l) the concentration of heavy metals in solution at any time, CA0 and CB0 the initial concentrations of heavy metals on adsorbent and solution, respectively, X_A the fractional conversion of metals and k_1 and k_2 are the first-order rate constants. At equilibrium conditions,

$$dC_B/dt = dC_A/dt \qquad (3)$$

and

$$X_{Ae} = \{Kc \; (C_{Bo}/C_{Ao})/Kc + 1\} \qquad (4)$$

where X_{Ae} is the fractional conversion of heavy metals at equilibrium and Kc is the equilibrium constant defined as follows,

$$Kc = C_{Be}/C_{Ae} = (C_{Bo} \; C_{Ao}\,X_{Ae}) / (C_{Ao} \; C_{Ao}\,X_{Ae}) = k_1/k_2 \qquad (5)$$

where C_{Be} and C_{Ae} are the equilibrium concentrations for heavy metals on the adsorbent and solution, respectively. The rate equation in terms of equilibrium conversion can be obtained from Eqs. (2), (4) and (5),

$$dX_A/dt = (k_1 + k_2)(X_{Ae} \; X_A) \qquad (6)$$

Integration of Eq. (6) and substituting for k_2 from Eq. (5), gives,

$$\ln (1 \; X_A/X_{Ae}) = k_1 (1 + 1/Kc) \, t \qquad (7)$$

Thus, Eq. (7) can be rewritten in a different form,

$$\ln[1 \; U(t)] = k'_r \, t \qquad (8)$$

where k'_r is the overall rate constant. Furthermore,

$$k'_r = k_1 (1 + 1/Kc) = k_1 + k_2 \qquad (9)$$

and

$$U(t) = (C_{Ao} \; C_A)/(C_{Ao} \; C_{Ae}) = X_A/X_{Ae} \qquad (10)$$

where $U(t)$ is called the fractional attainment of equilibrium. Figure 3.5(a) is shown as an example for these plots. Approximate linear fits were generally observed for all metal ions indicating that sorption reaction can be approximated to be of the first-order reversible kinetics. Correlation coefficients were found to be between 0.8509 and 0.9327, which means that there is a good agreement but not a perfect one.

Pseudo-first-order model

The sorption kinetics may also be described by a pseudo-first-order according to Ho and McKay [20] and Namasivayam and Kardivelu [21],

$$dq/dt = k'_1 (qe \; q) \qquad (11)$$

where qe is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q the amount of solute adsorbed at any time (mg/g) and k'_1 is

the adsorption constant. Eq. (11) is integrated for the boundary conditions t = 0 to >0 (q = 0 to >0) and then rearranged to obtain the following linear time dependence function,

$$\log (qe\ q) = \log (qe)\ (k'_1/2.303)\ t \qquad (12)$$

Figure 3.5(b) is shown as an example for these plots. Approximately, linear fits were observed for all metal ions indicating that sorption reaction can be approximated to first-order kinetics. Correlation coefficients were found to be between 0.8509 and 0.9327, which means there is also a good agreement as the first-order reversible reaction model.

Pseudo-second-order model

The rate constant for the adsorption of heavy metals on sawdust was determined by Lagergren equation. This equation modified by Ho and McKay [22-24] and the differential equation for this reaction is,

$$dq/dt = k'_2\ (qe\ q)^2 \qquad (13)$$

Integrating Eq. (13) for the boundary conditions t = 0 to >0 and q = 0 to >0 and rearranging to obtain the linearised form which is shown as follows,

$$t/q = (1/k'_2\ qe^2) + (1/qe)\ t \qquad (14)$$

$$h = k'_2\ qe^2 \qquad (15)$$

In these equations, h is the initial sorption rate (mg/g min). Figure 3.5(c) is shown as an example for these plots. Good fits were observed for all metal ions indicating that sorption reaction can be approximated with the second-order

kinetics model. The correlation coefficient in this case was 1.00, which is best than the previous two models.

The values of k'_2 of different metal ions were calculated from the slopes of the respective linear plots of t/q versus time and noted in Table 3.1. It may be concluded form the values of k'_2 of different metal ions that the reaction-taking place is of the pseudo-second order. The values of k'_2 also indicate the following preferential adsorption of different heavy metal ions [Pb(II) > Ni(II) > Cr(III) > Cu(II)] on saw dust. In a batch reactor with rapid stirring, there is also a possibility that the transport of adsorbate ions from solution into the pores of the adsorbent is the rate-controlling step [25]. This possibility was tested in terms of a graphical relationship between the amount of heavy metals adsorbed (mgg^{-1}) and the square root of time ($min^{1/2}$) and the results are showed in Figure 3.5(d) for different metal ions. It is clear from this Figure that these plots give straight lines of each metal ion but do not pass through the origin showing that the intraparticle diffusion is not the sole rate limiting factor for the adsorption of different metal ions [26]. The rate constant for intraparticle diffusion kp, of different metal ions was determined from the slopes of the respective plots and are given in Table 3.1.

The pore diffusion coefficient, $\overline{D}$ at room temperature of different metal ions was determined by using the following equation [27],

$$t_{1/2} = 0.03.r_0^2/\overline{D} \qquad (16)$$

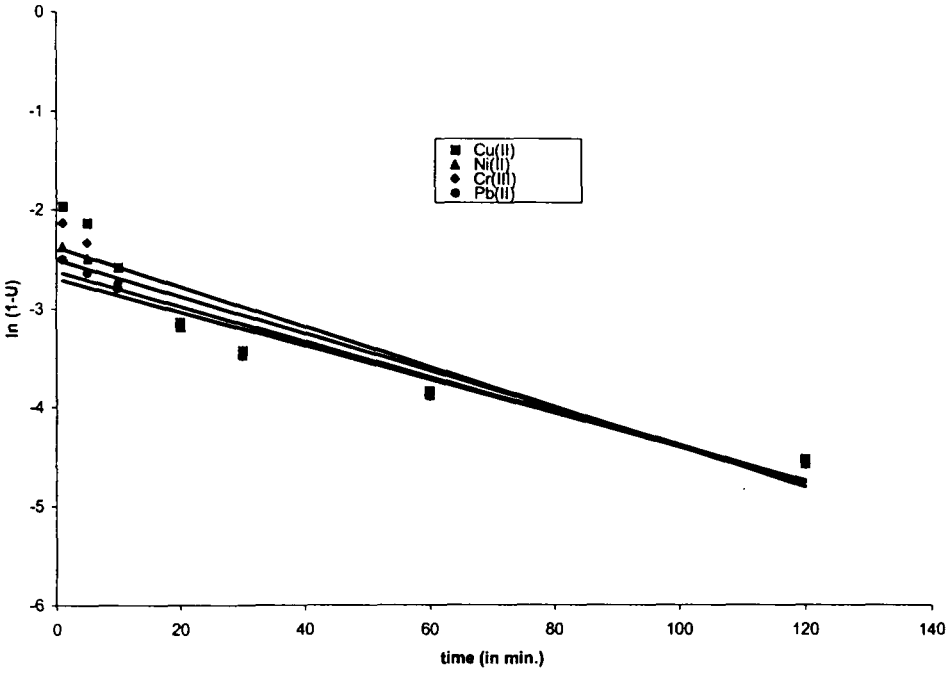


Figure 3.5(a). First-order reversible reaction kinetics plot for adsorption of different metal ions.

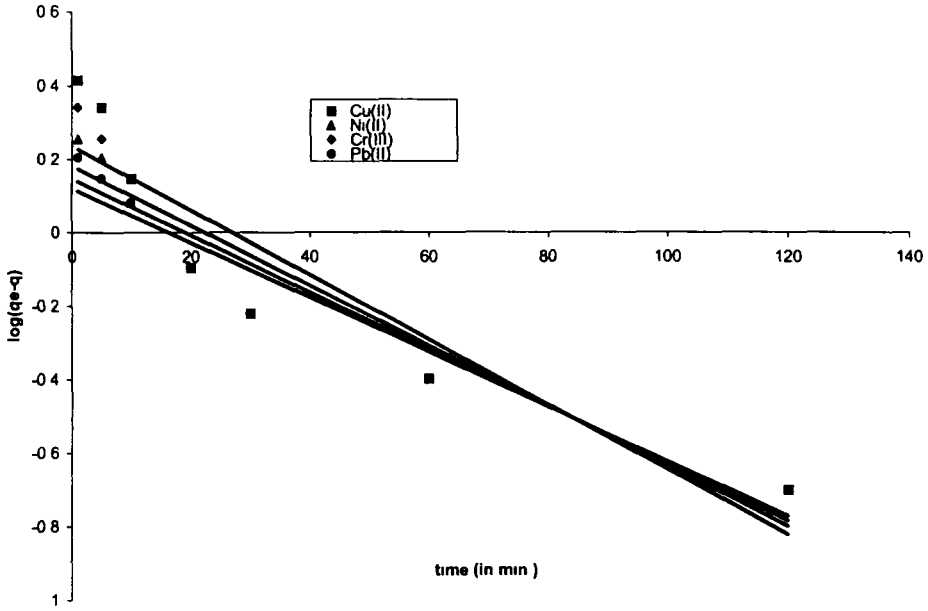


Figure 3.5(b). First-order kinetics plot for adsorption of different metal ions.

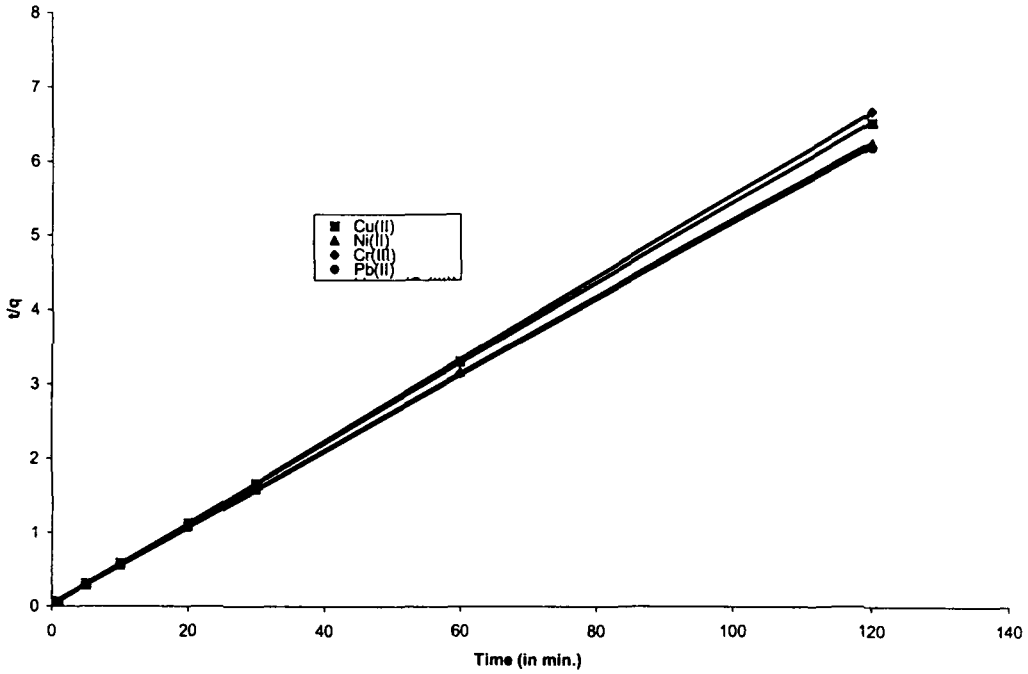


Figure 3.5(c). Second-order reaction kinetics plot for adsorpion of different metal ions.

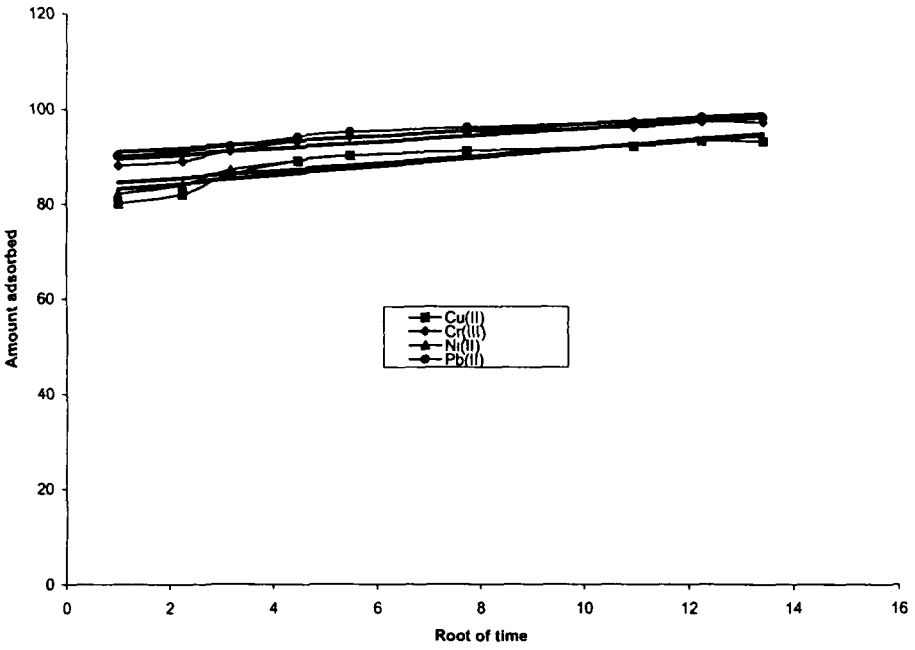


Figure 3.5(d). Plot of amount adsorbed versus square root of time for metal ions adsorption.

TABLE-3.1

Adsorption kinetic parameters of different metal ions on mango sawdust

Metal Ions	K'_2 in $gmg^{-1}min^{-1}$	Kp in $min^{1/2}$	$\overline{D}$ in cm^2sec^{-1}
Cu(II)	0.086913	0.9377	$3.34X10^{-11}$
Cr(III)	0.097923	0.6988	$3.34X10^{-11}$
Ni(II)	0.103837	0.7929	$3.34X10^{-11}$
Pb(II)	0.106159	0.6352	$3.34X10^{-11}$

where, $t_{1/2}$ (min) is the time for the adsorption of half amount of heavy metals, r_0 (cm) is the radius of adsorbent. The value of $\overline{D}$ in table was found in the order of 10^{-11} cm^2sec^{-1} indicating that the rate-controlling step is mainly intraparticle diffusion.

ADSORPTION ISOTHERM STUDIES

Batch adsorption studies were carried out by shaking 5.0 gm of the sawdust with 100 ml aqueous solution of different metals of desired concentrations at room temperature in different stoppared conical flask for different retention times using a temperature controlled shaker. At the end of predetermined time interval the adsorbent was removed by filtration and the equilibrium concentration was analyzed by atomic absorption spectrometer. Linear Regression analysis was done for fitting the Langmuir and Freundlich adsorption isotherms for the adsorption of different metal ions on the sawdust. The adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solution on to the mango sawdust follow the Langmuir isotherm as shown the high values of (R) in Table 3.2 for all these systems.

Langmuir equation: According to Langmuir model-

$$Ce/Am = 1/k.1/b + (1/b).\ Ce \qquad (17)$$

where Ce is the equilibrium concentration (mgL^{-1}) and Am is the amount adsorbed per specified amount of adsorbent (mgg^{-1}), k is the equilibrium constant and b is the amount of adsorbent required to form a monolayer. Hence a plot of Ce/Am versus Ce should be a straight line with a slope 1/b and intercept as 1/kb.

Langmuir adsorption isotherm of Cu(II), Cr(III), Ni(II) and Pb(II) ions at room temperature are presented in Figure 3.6{(a)-(d)}. It is evident from the figure that the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solution onto the sawdust fits well the Langmuir adsorption isotherm because of high correlation coefficient values. The values of k and b were calculated from the slope and intercept of the plots of Ce/Am versus Ce. The values of constants obtained for Langmuir isotherm are listed in Table 3.2.

TABLE-3.2

Related parameters for the adsorption of different metal ions on mango sawdust at room temperature

Metal Ions	Reg. Coeff.	Langmuir Constant	
	R	k	b
Cu(II)	0.997	3.96	90.09
Cr(III)	0.997	14.00	89.28
Ni(II)	0.998	17.50	95.23
Pb(II)	0.997	17.33	96.15

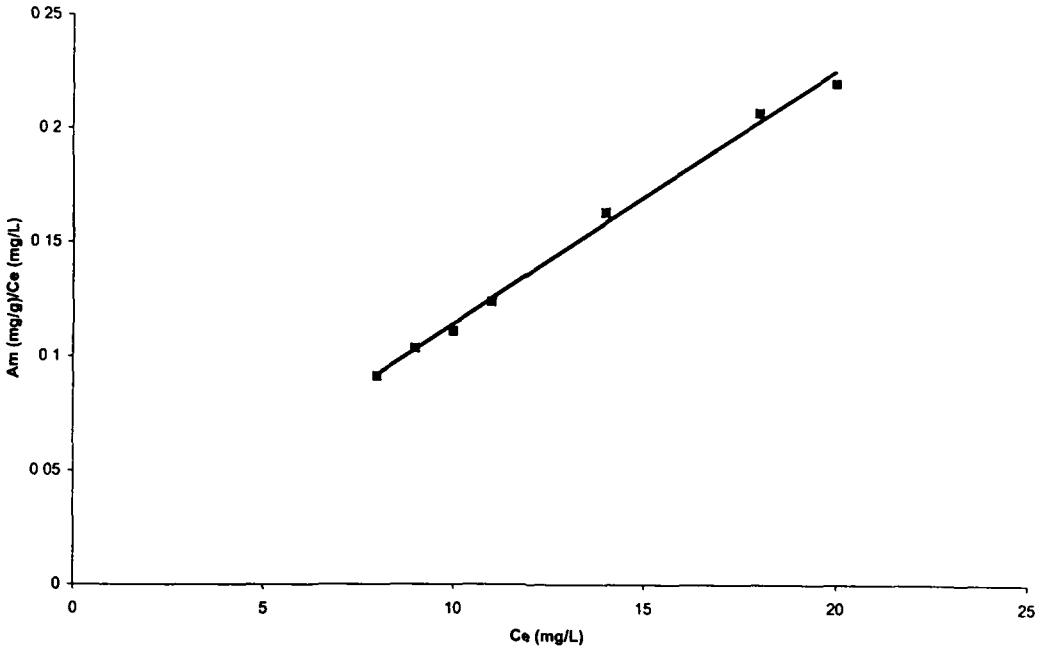


Figure 3.6(a). Langmuir adsorption isotherm of Cu(II).

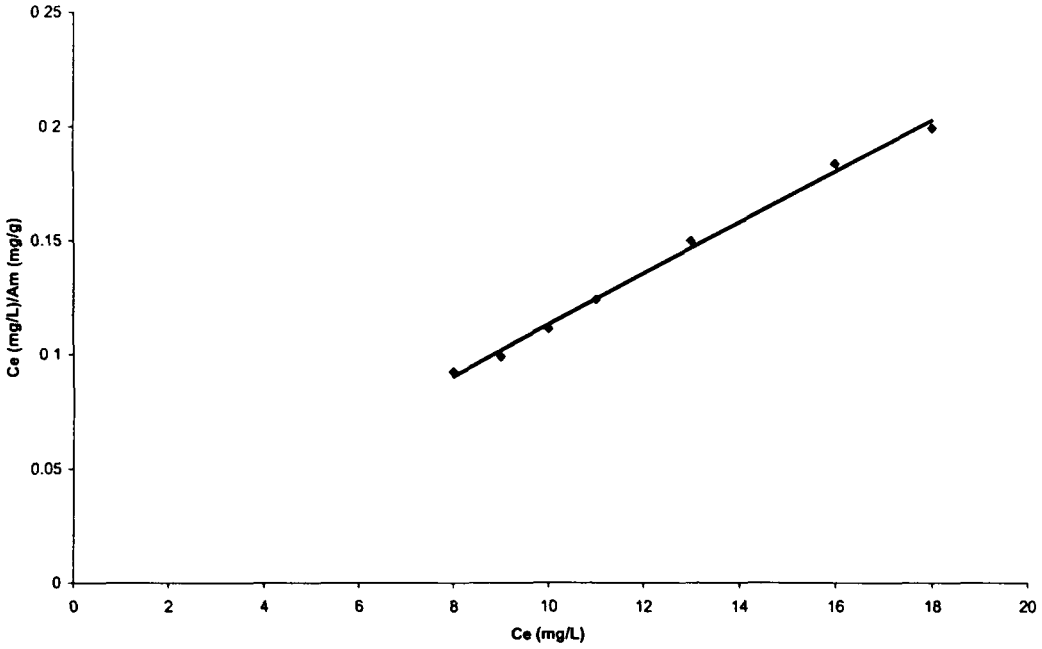


Figure 3.6(b). Langmuir adsrption isotherm of Cr(III).

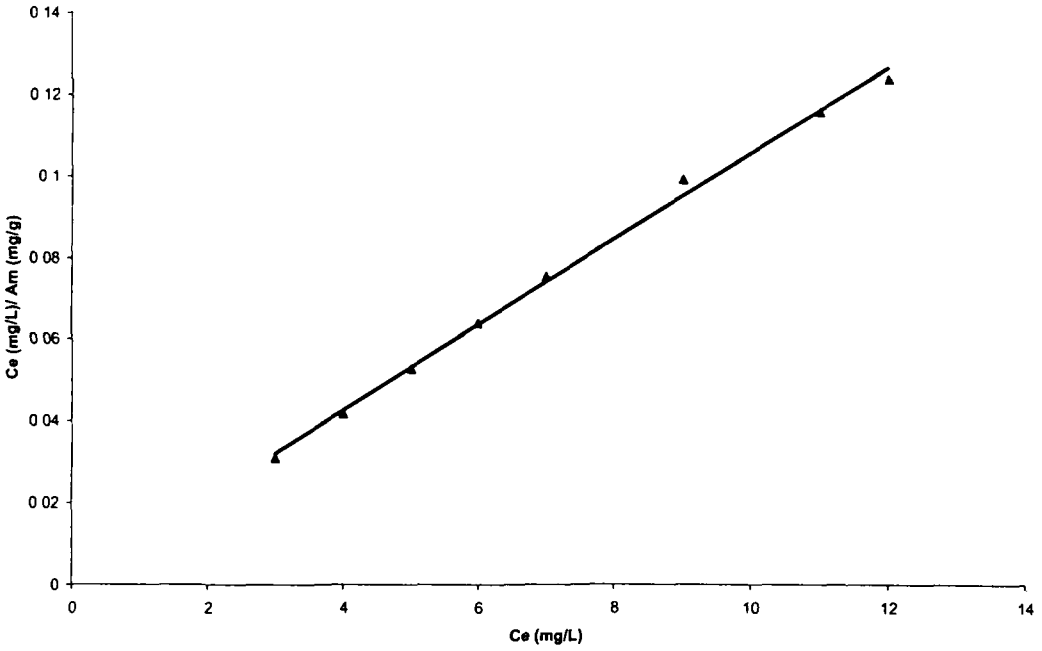


Figure 3.6(c). Langmuir adsorption isotherm of Ni(II).

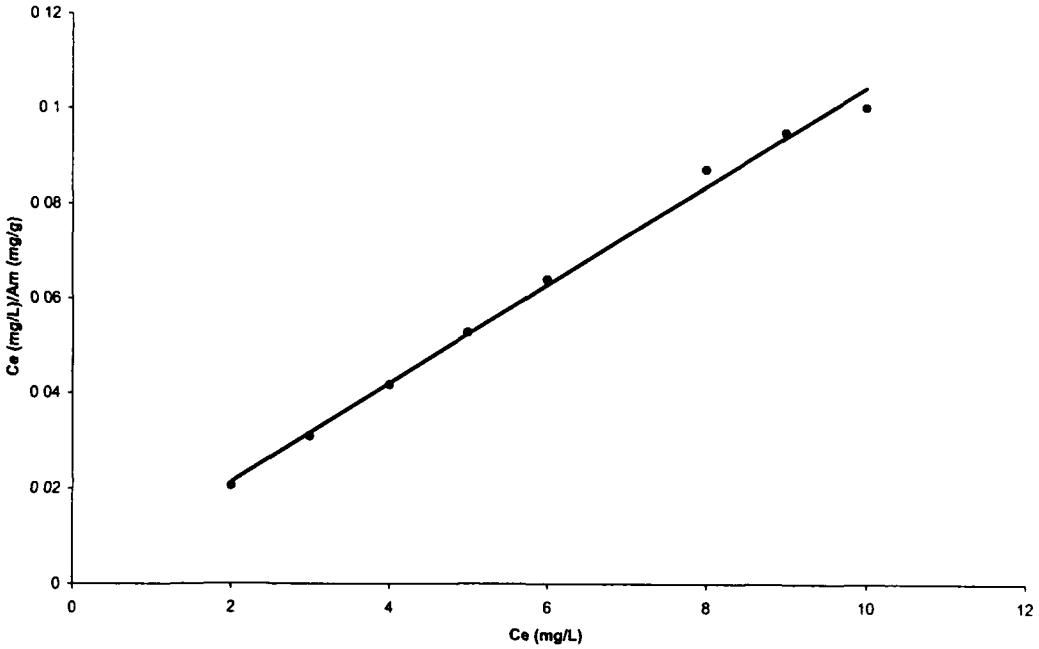


Figure 3.6(d). Langmuir adsorption isotherm of Pb(II).

REFERENCES

1. M. McCann, *Am. J. Ind. Med.*, **30**, 125 (1996).
2. M. Suzuki, *Water Sci. Technol.*, **35(7)**, 1-11 (1997).
3. K. Chandra Sekhar, S. Subramanian, J. M. Modak and K. A. Natarajan, *Int. J. Miner.Process.*, **53**, 107-120 (1998).
4. C. P. Huang and A. L. Morehart, *Water Res.*, **24(4)**, 433-439 (1990).
5. B. L. Summers, L. B. Gress, W. H. Philipp and S. B. Eastep, U.S., 11 pp., Cont.-in-part of U.S. Ser. No. 249, 733 (1995).
6. F. Franco, G. Prati and M. Pia, *Annali di Chimica* (Rome), **86(3-4)**, 125-132 (1996).
7. A. Mathur, S. K. Khare and D. C. Rupainwar, *J. Indust. Pollut. Control,* **5**, 52-57 (1989).
8. C. Faur-Brasquet, K. Kadirvelu and P. Le Cloirec, *Proceedings - Annual Conference, American Water Works Association*, 649-656 (2001).
9. R. Saravanane, T. Sundararajan and R. S. Sivamurthy, *Ind. J. Environ. Health*, **44(2)**, 78-87 (2002).
10. S. J. Park, Y. M. Kim and J. R. Lee, *Adsorpt. Sci. Technol.*, Proceedings of the Pacific Basin Conference, 3rd, Kyongju, Republic of Korea, May 25-29, 2003, 437-441 (2003).
11. S. K. Ouki and M. Kavannagh, *Water Sci. Technol.*, **39(10-11)**, 115-122 (1999).

12. G. L. Rorrer, T. Y. Hsien and J. D. Way, *Ind. Chem. Eng. Res.*, **32**, 2170 (1993).

13. S. K. Srivastava, A. K. Singh and A. Sharma, *Environ. Technol.*, **15**, 353 (1994).

14. B. J. W. Tuin and M. Tels, *Environ. Technol.*, **11(11)**, 1039-52 (1990).

15. Y. Hua and R. Gerald, *J. Microbios*, **90(363)**, 97-109 (1997).

16. Z. Yanfu, H. Yanyan and R. Gerald, *J. Environ. Monitoring and Assessment*, 33**(1)**, 61-70 (1994).

17. J. E. Hanway, R. G. Mumford and P. N. Mishra, *AIChE Symposium Series*, 75**(190)**, 306-14 (1979).

18. M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez, W. Geyer, J. Mattusch and R. Wennrich, *Colloid and Surfaces A: Physicochem. Eng. Aspects*, **219**, 243-252 (2003).

19. C. Namasivayam and K. Ranganathan, *Ind. Engg. Chem. Res.*, **34**, 869-973 (1995).

20. Y. S. Ho and G. McKay, *Trans. IChemE*, **76B**, 183-191 (1998).

21. C. Namasivayam and K. Kardivelu, *Carbon*, **37**, 79-84 (1999).

22. Y. S. Ho and G. McKay, *Proc. Biochem.*, **34**, 451-465 (1999).

23. Y. S. Ho and G. McKay, *water Res.*, **34**, 735-742 (2000).

24. Y. S. Ho, *J. Colloid Interface Sci.*, **262**, 307-308 (2003).

25. V. J. P. Poots, G. McKay and J. J. Healy, *Water Pollut. Control Fed.*, **50**, 926 (1978).

26. G. McKay, M. S. Otterburn and A. G. Sweeney, *Water Res.*, **14**, 15-20 (1980).

27. A. K. Bhattacharya and C. Venkobachar, *J. Environ. Engg. ASCe*, **110(1)**, 110-122 (1984).

CHAPTER – IV

COMPARATIVE STUDIES ON THE REMOVAL OF COPPER(II) IONS FROM AQUEOUS SOLUTIONS BY USING DIFFERENT ADSORBENTS

INTRODUCTION

Copper is introduced into natural waters through wastes from pulp paper, and paperboard mills, petroleum refining, and wool preserving industries and from copper smelters etc. [1]. An average concentration of copper in a copper wire mill wastewater has been reported to be 800 mg/L [2]. Municipal and storm water run-off also add large amounts of copper to the aquatic environment [3]. Water containing more than 1.0 mg/l of copper is not suitable for drinking purposes [4]. Excessive intake of copper results in its accumulation in the liver. The chronic copper poisoning is related to hemochromatosis and produces gastrointestinal catarrh when present in large amounts [5]. It is also toxic to fish life when it is present in natural waters even in low concentrations [6]. The methods for copper(II) removal from wastewater include precipitation [7], ion exchange, electrolysis and adsorption.

The adsorption processes for the removal of different pollutants have still been found to be economically appealing using suitable adsorbents and working at optimum conditions. Different adsorbents have been used in the past for the treatment of copper(II) rich effluent [8-9]. It has been reported that some aquatic plants [10-11], agricultural by-products [12], waste tea leaves [13] and sawdust [14-16] have the capacity to adsorb and accumulate heavy metals.

The use of activated carbon poses an economic problem for developing countries like India. The huge deposit of fly ash around thermal power plant poses

problem in its disposal. Sissoo sawdust has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to its abundance and easy availability. It is widely used for furniture making and the waste sawdust so produced is generally used as cooking fuel due to its negligible cost.

A survey of the present literature has shown that the workers in this field have not yet used the sissoo sawdust, which is a suitable and promising adsorbent.

The aim of the present work is therefore to study the removal of copper(II) using sawdust as the adsorbent. The results have also been compared using activated carbon and fly ash. The effects of retention time, pH of the solution, concentration and temperature have also been studied. The probable mechanism of copper(II) adsorption at solid-solution interface has also been worked out.

MATERIALS AND METHODS

ADSORBATE

A stock solution of copper(II) (0.01 M) was prepared by dissolving $CuCl_2.2H_2O$ (BDH, Analytical grade) in doubly distilled water.

ADSORBENTS USED

(i) Fly ash is a powdered material produced by the combustion of pulverized coal in thermal power plants. It was obtained from Kasimpur Thermal Power Plant, Aligarh (UP, India).

(ii) The sawdust of Sissoo tree (*Dalbergia sissoo*) was used as an adsorbent for the removal of Cu(II) from aqueous solution. It was collected from timber workshop near the University campus.

(iii) Activated carbon No. E4 34011 was obtained from E. Merck (INDIA) Ltd.

All the three adsorbents were washed with double distilled water filtered and dried at 105°C. After drying the adsorbents were sieved to 100-200 mesh size and used as such without prior treatment. The chemical composition of fly ash as determined by standard methods is given in Table 4.1.

APPARATUS

A digital pH meter (CP 901 model, India) was used for pH measurement; a high precession water bath incubator-shaker having a temperature variation of ±0.5°C was used for the equilibrium studies. A GBC 932 atomic absorption spectrometer (Australia), was used to determine the concentration of Cu(II) in solution.

TABLE-4.1

Chemical composition and characteristics of fly ash used

Constituents	(% by weight)	Constituents	(% by weight)
Si as SiO_2	56.40	Na_2O	1.20
Al as Al_2O_3	24.33	K_2O	0.72
Fe as Fe_2O_3	4.93	TiO_2	1.81
Ca as CaO	1.19	P_2O_5	0.24
Mn as MnO	---	Loss on ignition	6.87
Mg as MgO	2.59	Humidity	0.20

PROCEDURE

Batch operations were conducted in which aliquots of copper(II) solution of known concentrations were introduced into 100 ml stoppered glass bottles containing 0.5 g of the adsorbent per 50 ml of the solution of adsorbate. The bottles were shaken at room temperature (25°C) using an electric shaker for 2 h in order to attain equilibrium. The adsorbent was then removed by filtration. The equilibrium concentration, Ce of copper(II) was analyzed by atomic absorption spectrophotometer. A 1.0 N NaOH or HCl solution was used for varying the pH of copper(II) solution in order to study the effect of pH on the removal of Copper.

ADSORPTION MODEL

To quantify the adsorption capacity of all the three adsorbents viz.; fly ash, sawdust and activated carbon for the removal of copper(II) from water the Langmuir and Freundlich equations were applied:

Langmuir model-According to this model Langmuir proposed

$$Ce/Am = 1/k.\ 1/b + 1/b.Ce$$

where Ce is the equilibrium concentration (mol/l) and Am is the amount adsorbed per specified amount of adsorbent (mg/g), k is the equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence a plot of Ce/Am versus Ce should give a straight line with a slope 1/b and intercept as 1/k.b.

Freundlich model- According to this model

$$Am = k.\ Ce^{1/n}$$

or

$$\ln Am = \ln k + 1/n.\ln Ce$$

where all their terms have the usual significance and 'n' is an empirical constant. Thus a plot of ln Am versus ln Ce should give a straight line with a slope of 1/n and intercept ln k. This model deals with the multilayer adsorption of the substance on the adsorbent. The plots of Ce/Am versus Ce and ln Am versus ln Ce are in Figures 4.5-4.7. The points indicate the observed data and the lines correspond to the fitted data.

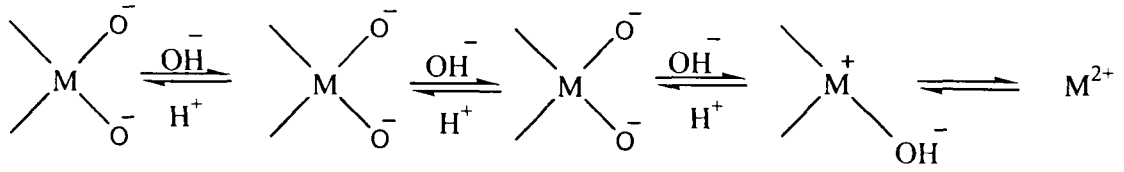
RESULTS AND DISCUSSION

TIME OF EQUILIBRATION

The variation of adsorption of Cu(II) with time is shown in Figure 4.1. The equilibrium was attained after shaking for 1.5 hrs in case of sawdust and activated carbon and 2 hrs in case of fly ash. Therefore, for all experiments the optimum shaking period was taken as 2 h. The difference in attainment of equilibrium for fly ash is most probably due to the difference in structural composition and surface area.

EFFECT OF pH

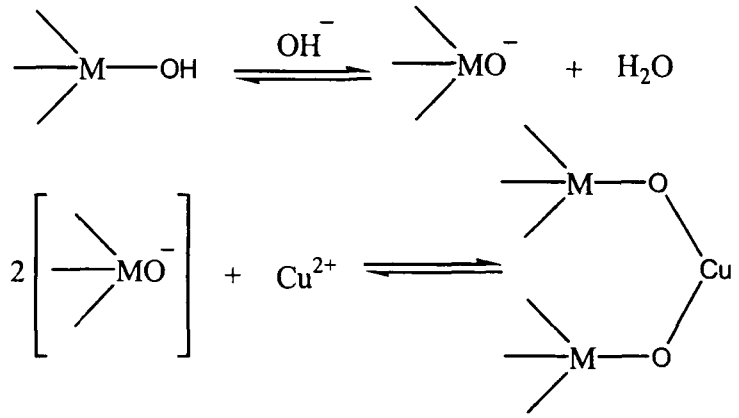
The effect of pH on the adsorption of Cu(II) is given in Figure 4.2. It shows that below pH 4, the adsorption of copper(II) is insignificant on fly ash, sawdust and activated carbon. In case of all the three adsorbents the per cent adsorption increases with increasing pH up to certain value and then decreases slightly with further increase of pH. The maximum adsorption took place around pH 6.0 in all cases. The variation in extent of removal of Cu(II) with pH of the solution may be explained on the basis of ion exchange mechanism. The metal oxides present in the adsorbent make aquocomplexes in the presence of water dipoles and develop positively or negatively charged surface through amphoteric dissociation at varying pH values [17] in the following manner:



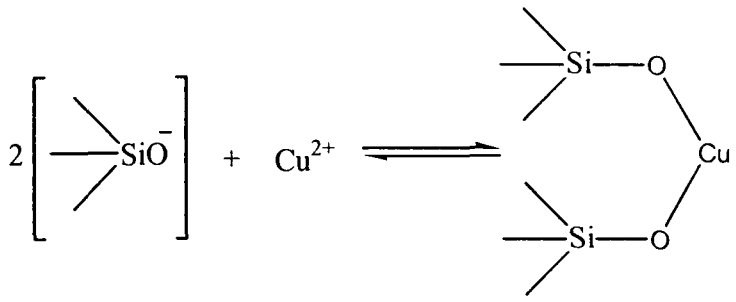
(Basic dissociation) (Acid dissociation)

where, M stands for Si, Al etc.

The zero point charge thus developed in acidic medium does not favour the association of cationic adsorbate species. However, beyond pH 3 the adsorbent surface gradually starts to become negatively charged which offers the suitable sites for the adsorption of copper(II) as follows:



The pH_{zpc} for alumina and silica has been reported 8.2 and 2.3 respectively [18]. The change in solubility of alumina with pH shows a maxima near the neutral pH region, whereas in the case of silica the change is not pronounced [17]. This suggests that a relatively small number of alumina sites will be available for the adsorption of copper(II) at pH > 6.0. Thus the major scheme for the adsorption of Cu(II) may be written as:



However, at lower pH, the interaction of copper(II) ions with alumina sites are also likely to occur as follows:

The decreasing trend of adsorption above pH 6.0 may be due to the formation of soluble hydroxy complexes.

According to Baes and Mesmer [19], as the solution pH is increased, the onset of metal hydrolysis and precipitation began at pH > 6 for copper. As solution pH is increased the onset of adsorption therefore occurs before the beginning of hydrolysis. The onset of adsorption occurred at a lower pH than the beginning of hydrolysis, which agrees with earlier work on adsorption of some metals on $Si0_2$ and $Ti0_2$.

EFFECT OF pH ON DESORPTION

The results presented in Figure 4.2 show that the extent of desorption of Cu(II) from the adsorbents increases by decreasing the pH of the solution from 6.0 to 1.0 at 25°C. An approximately linear relationship is obtained for the amount adsorbed and the pH of the aqueous suspension, which is similar to the findings of other workers [20].

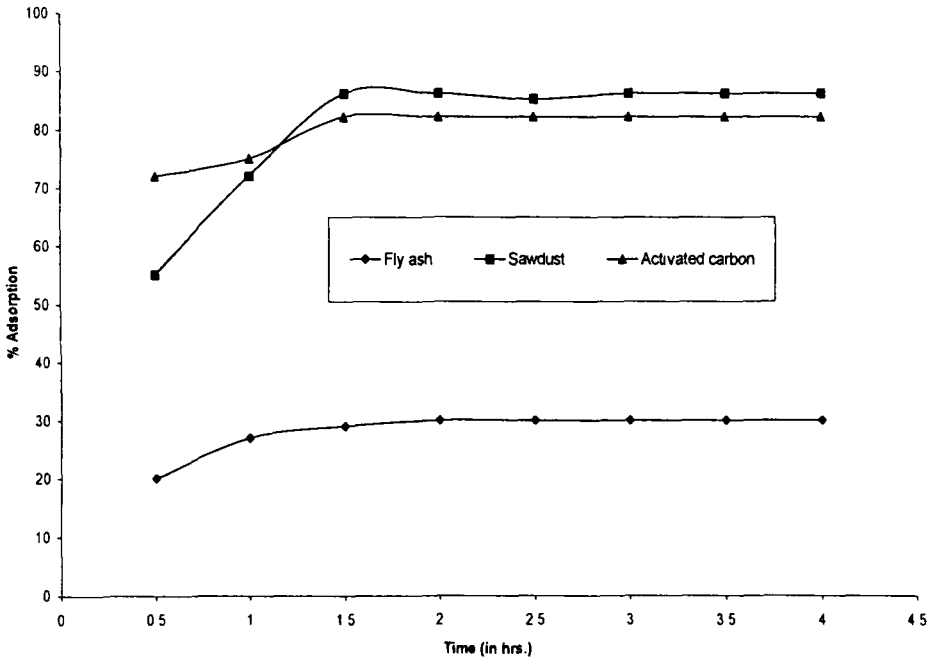


Figure 4.1. Effect of time on the adsorption of Cu(II).

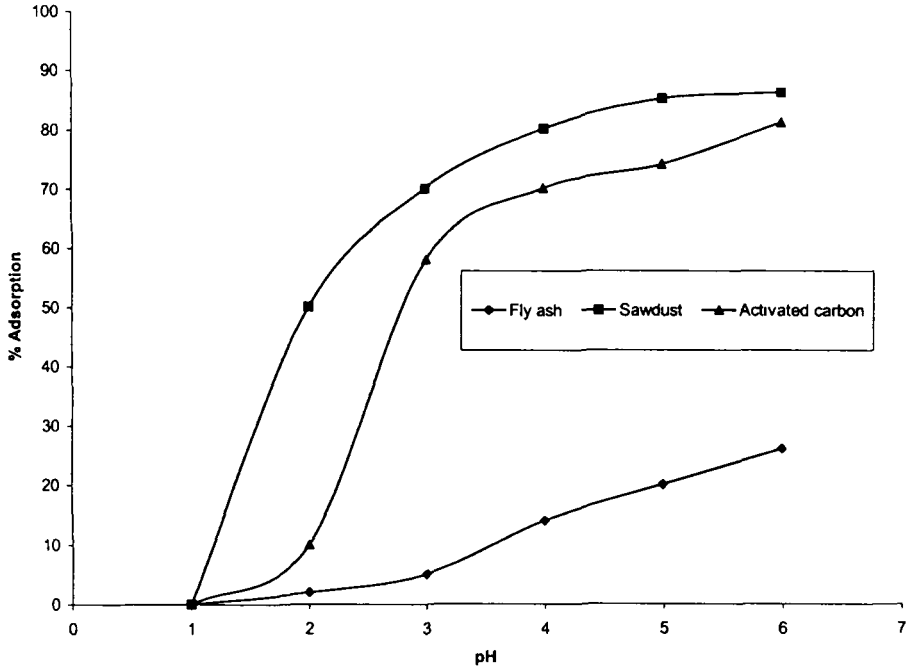


Figure 4.2. Effect of pH on the adsorption of Cu(II).

The rate of desorption of copper(II) from the adsorbent is slow from pH 6.0 to 3.0 but fast desorption was observed from pH 3.0 to 1.0 so much so that 100% copper(II) was desorbed from the adsorbent at pH 1. Probably in the former range of pH, desorption of physically adsorbed species is the major phenomena while in the later range, the chemisorption accompanied with ion exchange is the dominating process as suggested by Choudhury and Vaidya [21].

EFFECT OF TEMPERATURE

The adsorption of copper(II) on fly ash from 25-50^{0}C is passing through a maxima at 30^{0}C as shown in figure 4.3. The enhanced adsorption might be due to the desolvation of the adsorbing species, changes in the size of the pores and enhanced rate of intraparticular diffusion of adsorbate [22]. But after 30°C, desorption of the adsorbate increases leading to a net decrease in adsorption from 30-50°C. The percent adsorption decreases sharply above 40°C due to enhanced rate of desorption. The decreasing trend of adsorption with temperature in the case of fly ash is mainly due to the weakening of adsorptive forces between the active sites of fly ash and the adsorbate species, and also between the adjacent molecules of adsorbed phase [18]. The extent of decrease in adsorption of solute of definite concentration with increase in temperature depends on the nature of the adsorbate-adsorbent system. In the case of sawdust and activated carbon, the percent adsorptions remain almost equal and constant between 25-40^{0}C. Above 40^{0}C, the percent adsorption decreases in both the cases so much so that the adsorption

capacity of sawdust and fly ash becomes equal at 50^0C but that of activated carbon remains slightly higher as shown in figure 4.3.

The constant adsorption capacities of sawdust and activated carbon in a specific temperature range suggests that probably the surface adsorption as well as the ion exchange process of copper on these two adsorbents occur simultaneously. With the rise in temperature, the desorption of copper(II) ion due to enhanced kinetic energy is compensated with the enhanced rate of ion exchange. But the former process overcomes the later one above 40°C leading to net decrease in percent adsorption.

EFFECT OF CONCENTRATION

The effect of initial concentration of solute (copper) at pH 6.0 and 25°C on the adsorption process is shown in Figure 4.4. It was found that:

(i) More than 98% copper was removed by sawdust in the concentration range 1 x 10^{-4} M (17.054 mg/L) to 1 x 10^{-3} M (170.54 mg/L).

(ii) Up to 95% copper(II) was removed in concentration below 4 x 10^{-4}M (68.216 mg/L) and about 85% removal was achieved in the concentration range between 4 x 10^{-4} M to 1 x 10^{-3} M by activated carbon.

(iii) Fly ash has been found suitable for the removal of more than 80% copper in lower concentration range only (< 1 x 10^{-4} M).

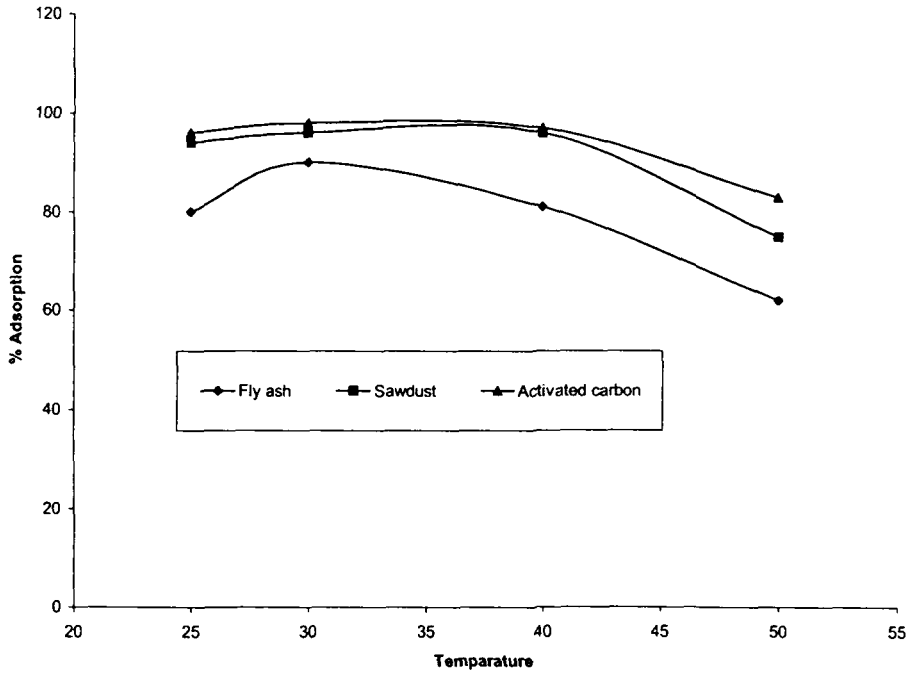


Figure 4.3. Effect of temparature on the adsorption of Cu(II).

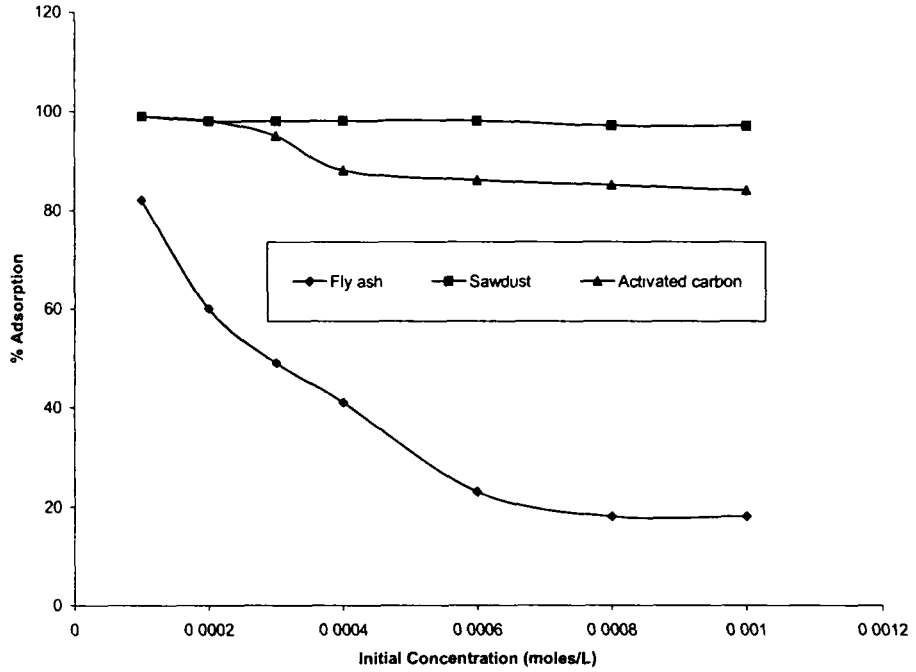


Figure 4.4. Effect of initial concentration on the adsorption of Cu(II).

ADSORPTION ISOTHERM

The parameters related for fitting of Freundlich as well as Langmuir equations are given in Table 4.2 for comparison. The isotherm plots for all the three adsorbents are shown in Figures 4.5-4.7.

Freundlich adsorption isotherm is obeyed by activated carbon whereas Langmuir type adsorption process is followed in case of fly ash. However, sawdust shows close resemblance between both types of adsorption processes which is evident from the values of the regression coefficients of fittings, R. Further, the shapes of both the adsorption isotherms are unique in their features. Also the values of R are sufficiently lower than those of activated carbon and fly ash as well as farther from unity. This indicates that besides surface adsorption some other mechanisms of uptake are prevailing sufficiently in sawdust and responsible for the enhanced uptake capacity of this material for copper(II).

It has already been noted earlier, that this process is highly prone to pH [23]. Actually $H^+$and OH^- ions are the potential determining lattice ions for various inorganic salts. Foxall et al. [24] have shown that the pH may have a role secondary to that of the fundamental potential determining lattice ions, simply serving to control the solution equilibrium between free potential determining ions and those in the form of solution complexes.

The charging mechanism [25] of inorganic oxides such as SiO_2, TiO_2, and Al_20_3 relies on the presence of ionizable groups on the solid surface, these being

assumed to be amphoteric hydroxylated groups. The charging mechanism can ideally be represented as:

$$MOH_2^+ \overset{H^+}{\rightleftharpoons} MOH \overset{H^+}{\rightleftharpoons} MO^-$$

KINETICS OF THE ADSORPTION PROCESS

When the solution containing Cu^{2+} ions is shaken, the adsorbate species (Cu^{2+}ions) is transported to the solid phase by intraparticle transport phenomena [26]. The intraparticle transport is supposed to be the rate-controlling step. The rate of particle transport through this mechanism is slower than adsorption on exterior surface site of the adsorbent. The amount of adsorbed species varies proportionately as a function of retention time and is given by the equation:

$$\log x = \log k_t + m.\log t$$

where 'x' is the % adsorption, 't' is the shaking period in hours, 'm' is the slope of the linear plot, and 'k_t' is constant coefficient. The deviation of the line from origin indicates that intraparticle transport is not the only rate-limiting step.

Probably, the transport of the adsorbate (copper) from the solution through the particle solution interface, into the pores of the particles as well as the adsorption on the available surface of the adsorbents (i.e., fly ash, sawdust and activated carbon) are both responsible for adsorption.

TABLE 4.2

The related parameters for the fitting of Langmuir and Freundlich equation at room temperature

Adsorbents	Reg. Coeff.	Langmuir Constants		Reg. Coeff.	Freundlich Constants	
	(R)	K	b	(R)	K	1/n
Fly ash	0.98	29981	0.001	0.95	0.0029	0.147
Sawdust	0.86	121366	0.009	0.85	23.625	0.725
Activated carbon	0.97	57603	0.005	0.98	0.1480	0.3814

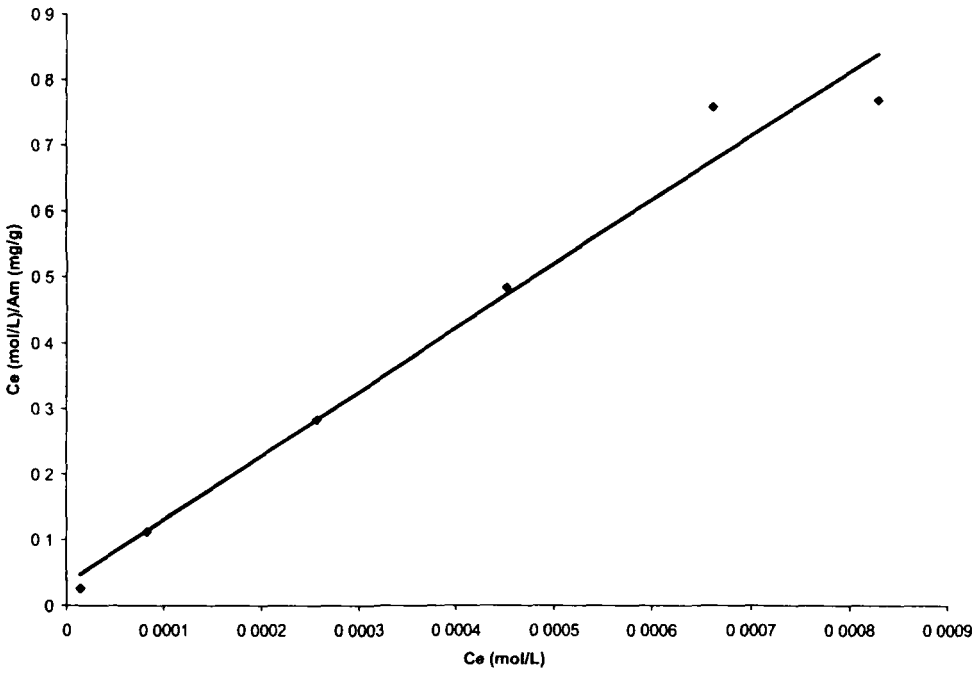


Figure 4.5 (a). Langmuir plot for the adsorption of Cu(II) on fly ash

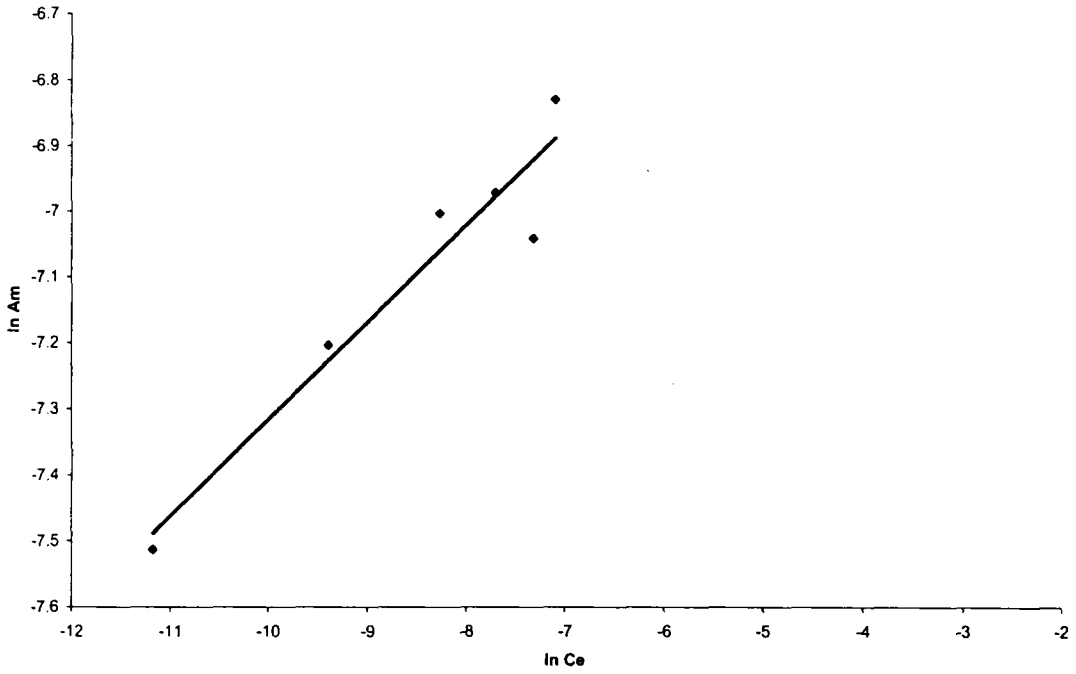


Figure 4.5(b). Freundlich plot for the adsorption of Cu(II) on fly ash

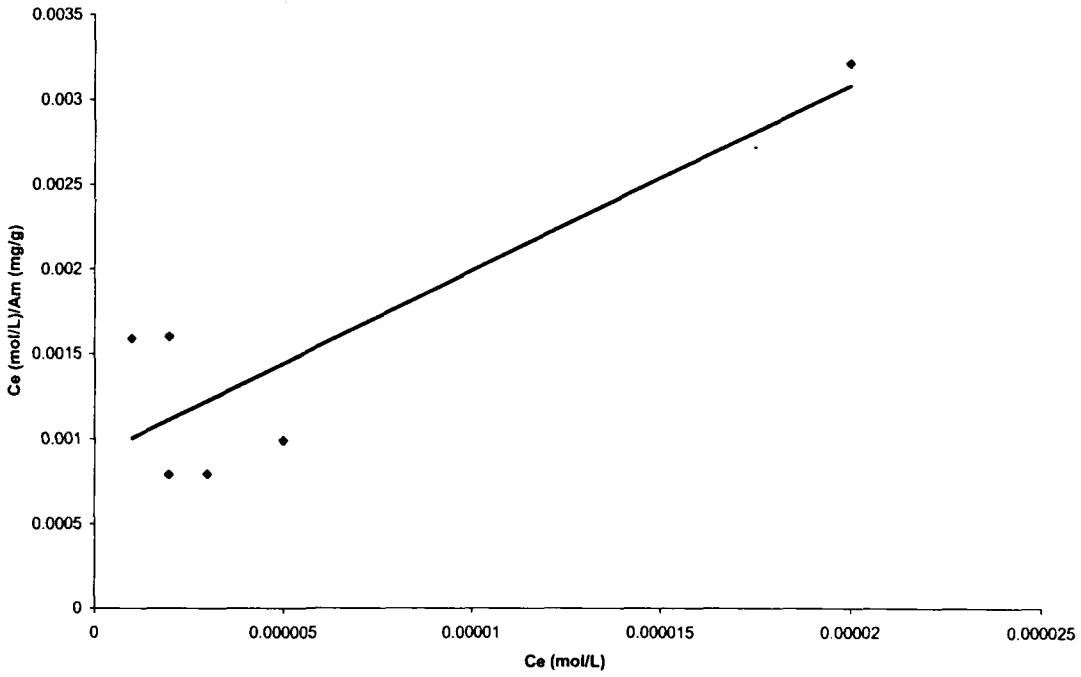


Figure 4.6(a). Langmuir plot for the adsorption of Cu(II) on sawdust

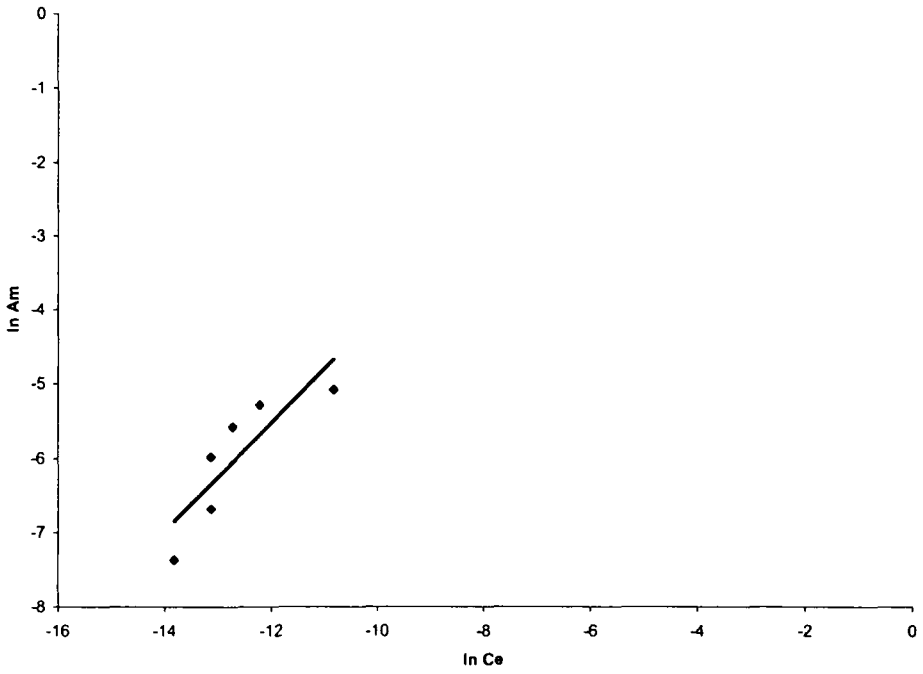


Figure 4.6(b). Freundlich plot for the adsorption of Cu(II) on sawdust

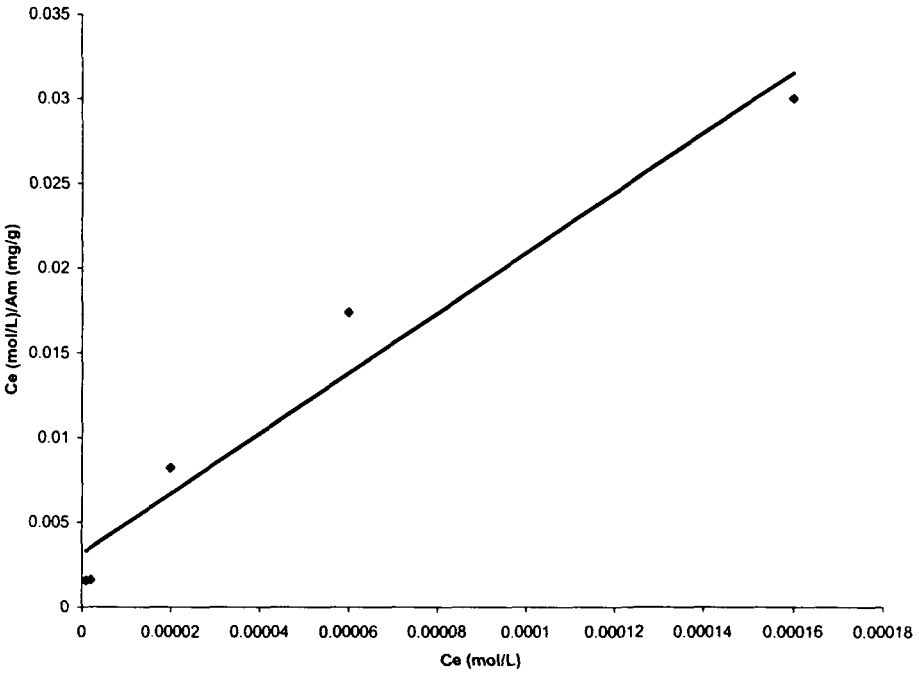


Figure 4.7(a). Langmuir plot for the adsorption of Cu(II) on activated carbon

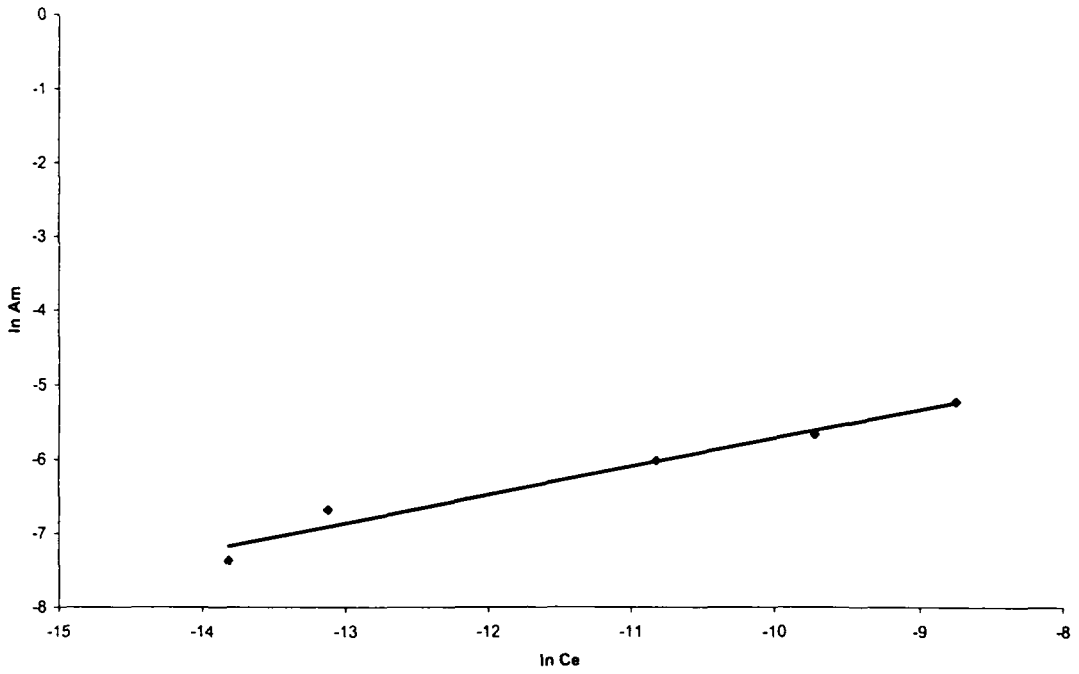


Figure 4.7(b). Freundlich plot for the adsorption of Cu(II) on activated carbon

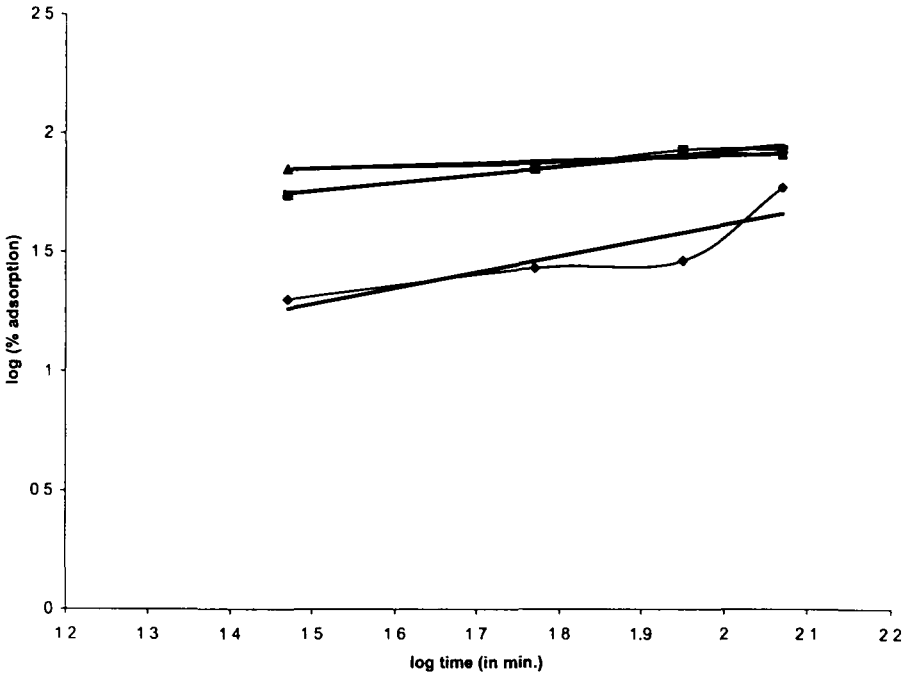


Figure 4.8. Kinetics of Cu(II) adsorption.

REFERENCES

1. K. K. Panday, P. Gur and V. N. Singh, *Water Res.*, **19(7)**, 869-873 (1985).
2. K. K. Panday, G. Prasad and V. N. Singh, *Water Air Soil Pollut.*, **27**, 287-296 (1986).
3. G. C. Gupta and F. L. Harrison, *Pollut. Res.*, **1**, 1 (1983).
4. C. S. Rao, *Environmental Pollution Control Engineering*, pp 313-329. Wiley Eastern Limited, New Delhi, (1992).
5. WHO: *Guide lines for Drinking Water Quality,* World Health Organisation, Geneva, Switzerland, Vol. **2**, p 263 (1984).
6. R. T. Camp, *Water and its impurities*, 2nd Edition Reinhold, New York, (1964).
7. M. Suzuki, *Water Sci. Technol.*, **35(7)**, 1-11 (1997).
8. H. A. Elliot and C. P. Huang, *Water Res.*, **15**, 849 (1981).
9. G. C. Gupta and F. L. Harison, *Water Air Soil Pollut.*, **17**, 357 (1982).
10. A. K. De, A. K. Sen, D. P. Modak and S. Jana, *Water Air Soil Pollut.*, **24**, 351 (1985).
11. G. Fajardo and C. Alberto, *Rev. Colomb Quin.*, **14(1-2)**, 89-97 (1987).
12. D. Mohan and K. P. Singh, *Water Res.*, **36**, 2304-2318 (2002).
13. T. Tanweer and K. R. Majid, *Environ. Technol. Lett.*, **9**, 1223-1232 (1988).
14. Y. S. Chung, K. W. Lee, Y. S. Yoon, S. H. Kwon and K. S. Lim, *Bull. Korean Chem. Soc.*, **13**, 212-214 (1992).

15. M. Ajmal, A.H.Khan, S. Ahmad and A. Ahmad, *Water Res.*, **32(10)**, 3085-3091 (1998).

16. B. Acimioglu and M. H. Alma, *Holz als Roh und Waterstoff.*, **62(4)**, 268-272 (2004).

17. K. K. Panday, G. Prasad and V. N. Singh, *Indian J. Chem.*, **23A**, 514-515 (1984).

18. K. P. Yadava, B. S. Tyagi, K. K. Panday and V. N. Singh, *Environ. Tech. Lett.*, **8**, 225-234 (1987).

19. G. B. Beas and R. E. Mesmer, *Hydrolysis of Cations* John Wiley and Sons, New York, (1976).

20. C. P. Huang and P. K. Wirth, *J. Environ. Engg. Div. Am. Soc. Civ. Engg.*, **108**, 1280 (1982).

21. G. R. Chaudhry and S. H. Vaidya, *J. Chem. Technol. Biotechnol.*, **32**, 883 (1982).

22. W. R. Knocke and L. H. Hemphill, *Water Res.*, **15**, 275 (1981).

23. L. C. Bell, A. M. Posner and J. P. Quirk, *J. Colloid Interface Sci.*, **42**, 250 (1973).

24. T. Foxall, G. C. Pterson, H. M. Rendall and A. L. Smith, *J. Chem. Soc. Faraday Trans.* **175**, 1034 (1979).

25. G. D. Parfitt and C. H. Rochester, *Adsorption from solution at the solid/liquid interface* p. 252, Academic Press Inc. (London) Ltd, (1983).

26. W. J. Jr. Weber and J. C. Morris, *San. Engg. Div. Am. Soc. Civ. Engg.*, **89**, 31 (1963).

CHAPTER – V

REMOVAL OF ARSENIC(III) FROM AQUEOUS SOLUTIONS THROUGH ADSORPTION ON ACTIVATED CARBON

INTRODUCTION

Pollution is now an important problem owing to increased industrialization and population overflow, and much effort is directed towards its control. Use of adsorbents, particularly activated carbon, is of current interest in the removal of pollutants from air and water. Increasingly strict discharge limits on heavy metals and their widespread uses, threatening presence at hazardous waste sites have accelerated the search for advanced and economically attractive treatment technologies for their removal. Adsorption processes are promising in this regard as opposed to more conventional chemical precipitation in that way achieve higher level removals over a wider range of solution conditions.

Arsenic is of environmental concern due to its toxicity and carcinogenicity. It is widely distributed in the biosphere. Drinking water has identified as one of the major sources of arsenic exposure by the general population [1-2]. Concerns over possible health risks associated with the chronic ingestion of low levels of arsenic in drinking water have also been increased [3]. In natural water, arsenic is primarily present in a variety of chemical forms, including, several mono-, di-, tri methylated arsenic compounds and inorganic arsenic(III) and arsenic(V). Arsenic(V) is the major arsenic species in surface water, while arsenic(III) is the dominant species in ground water. Both elemental arsenic and arsenic(V) are markedly less toxic than arsenic(III). Further the toxicity of such compounds decreases in the order arsine > arsenite > arsenate > alkyl arsenic acids > arsonium

compounds and metallic arsenic [4]. The toxic effects of arsenic on human beings are summarized in Table 5.1 [5].

TABLE-5.1

The toxic effects of arsenic on human beings

Affected area	Toxic effect
Skin	Hyper pigmentation, hyperkeratosis, black foot disease, gangrene, skin cancer
Lung	Lung cancer (needs confirmation)
Liver	Cirrhosis, haemongioendothelioma
Kidneys	Renal read sorption problems
Blood system	Inhibits biosynthesis of porphyrin, effects white blood cells
Reproduction system	Spontaneous abortions
Peripheral nervous system	Peripheral neuropathy, paralysis, loss of hearing
Gastrointestinal tract	Damage of intestine, intestine pain

A variety of treatment processes have been studied for arsenic removal from water. The major technologies include precipitation-coagulation, membrane separation, ion exchange and adsorption [6-8]. The precipitation-coagulation technique is generally costly, not suitable for small water facilities, and less effective for removal of arsenic(III). Membrane separation processes are more effective in removing arsenic(V) than arsenic(III). Similarly ion-exchange is more effective in removing Arsenic(V) than arsenic(III), because arsenic(V) is normally present as an anion in the medium-pH range while arsenic(III) exists as uncharged molecules in water. Adsorption methods for the removal of arsenic are diversified according to the adsorbents used.

In recent years, the cost effective adsorbents reported for the removal of toxic metals from aqueous solution are, clay [9], sawdust [10-11], fly ash [12-13], groundnut husk [14], rice husk [15], coconut husk [16], gel sorbent [17], zeolites [18-19], ion-exchanger [20-21].

Out of them activated carbon have been successfully employed as adsorbents due to their well developed porous structures and large internal surface comprised of hydrophobic grapheme layers and hydrophilic surface functional groups. These porous materials can be used for the adsorption of a wide range of species from both gas and liquid phases. An important aspect in the treatment of aqueous systems using active carbons is that it can be used to remove both

inorganic and organic species and thus it very important in the purification of water.

Many forms of activated carbons have been used for a long time in numerous processes of gas, water, and wastewater purification. Since the compositions of activated carbon vary considerably depending upon its source and method of treatment and so does the extent of adsorption so we have selected the less used activated carbon No. E4 34011 and studies the adsorption of arsenic(III) on it and is reported here in this manuscript. The appropriate thermodynamic parameters have also been calculated and discussed.

MATERIALS AND METHODS

REAGENTS AND CHEMICALS

Activated carbon No. E4 34011 was obtained from E. Merck (INDIA) Ltd. Solid sodium arsenite, $NaAsO_2$ was obtained from (Merck). The characteristics of the activated carbon are summarized in Table 5.2. All other reagents used were of analytical grade.

APPARATUS

A high precession water bath incubator-shaker having a temperature variation of ±0.5°C was used for the equilibrium studies. A GBC atomic absorption spectrometer, Australia, with hydride generation facility was used to determine the concentration of arsenic(III) in solution.

PRELIMINARY TREATMENT OF ACTIVATED CARBON

The activated carbon was used after drying at 110°C for 3 hours. It was treated with 1M HCl solution for 2 hours. It was then washed with double distilled water repeatedly until free from chloride ions. Finally it was dried at 110°C. The dried activated carbon was then stored in a dessicator over anhydrous P_2O_5.

SOLUTION OF ARSENIC(III)

Analytical reagent grade solid sodium arsenite, $NaAsO_2$ was dissolved in limited quantity of double distilled water. Later the quantity was made up to one liter with the addition of double distilled water.

TABLE-5.2

Characteristics of activated carbon

S. No.	Characteristics	Results
1	Surface area*	$910m^2/g$
2	Bulk density*	$0.62g/Cm^3$
3	Pore volume*	$0.75g/Cm^3$
4	Moisture	6.8%
5	Ash content	6.6%
6	Substances soluble in water*	1%
7	Substances soluble in acid*	3%
8	Ion exchange capacity	Nil
9	Lead (Pb)*	0.005%
10	Iron (Fe)*	0.1%

* Information furnished by supplier

ADSORPTION STUDIES

Samples weighing 0.5 gm of the purified activated carbon were shaken with 50 ml arsenic(III) solutions of different concentration at 22, 45 and 60°C for different times using a temperature controlled shaker. Preliminary studies have shown that equilibrium is reached after 120 minutes. After the predetermined time interval the equilibrating solutions were filtered and analyzed by atomic absorption spectrometer, having the hydride generation facility, to determine the equilibrium concentration (Ce) of arsenic(III) in the solutions. The amount of arsenic(III) in mmole/gm activated carbon (Am) was calculated from the difference of initial concentration (Ci) and the final concentration of arsenic(III) in the solution.

TREATMENT OF DATA

A. To determine the shapes isotherms, the Am values were plotted as a function of Ce at different temperatures. The plots are shown in figure [5.3].

B. A computer simulation technique was used to fit the adsorption data for the following adsorption models-

Langmuir model- According to this model-

$$Ce/Am = 1/k.1/b + 1/b.Ce \qquad (1)$$

where Ce and Am are the same parameter as mentioned earlier. k is the equilibrium constant and b is the amount of adsorbate required to form a

monolayer. Hence a plot of Ce/Am versus Ce should give a straight line with a slope 1/b and an intercept 1/kb as shown in Figure [5.4].

Freundlich model- According to this model-

$$\ln Am = \ln k + 1/n.\ \ln Ce \qquad (2)$$

where all the term have their usual significance and n is an empirical constant. Thus a plot of ln Am versus ln Ce should give a straight line with slope 1/n and intercept ln k.

C. Thermodynamic parameters ΔG, ΔS and ΔH were calculated from the equations given below:

The free energy change (ΔG) was calculated from the relation,

$$\Delta G = - RT \ln k \qquad (3)$$

Similarly the enthalpy change (ΔH) was calculated from the following equation,

$$\ln k = -\Delta H/RT + C \qquad (4)$$

and the entropy change (ΔS) was calculated from the equation

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

RESULTS AND DISCUSSION

TIME OF EQUILIBRIUM

The dependence of adsorption of arsenic(III) from solution on activated carbon with time is presented in Figure 5.1. The adsorption increases with increasing contact time and the equilibrium was attained after shaking for 30 minutes at 25°C in pure aqueous medium. The maximum uptake after this time is constant at a value 84%. However, the time of equilibrium used in all the following studies was set to 120 minutes for the sake of simplicity as well as to ensure the complete process of adsorption.

EFFECT OF DOSE ON THE ADSORPTION PROCESS

The effect of dose of activated carbon on the adsorption of arsenic(III) is presented in Figure 5.2. The data indicates that the adsorption increases with the increase in the dose of activated carbon probably due to its high surface area. The maximum uptake exhibited at 600 mg of adsorbent in an aqueous medium.

ADSORPTION ISOTHERM STUDIES

The adsorption of arsenic(III) on activated carbon has been studied at different temperatures (25, 45 and 60°C) in aqueous medium. Langmuir adsorption model appears to be the best fit as shown in Figure 5.3. The values of regression coefficients are close to unity for this model as compared to those for Freundlich adsorption model. The values of k and b were calculated from the slope and intercept of the plot of Ce/Am versus Ce. The constant values obtained from

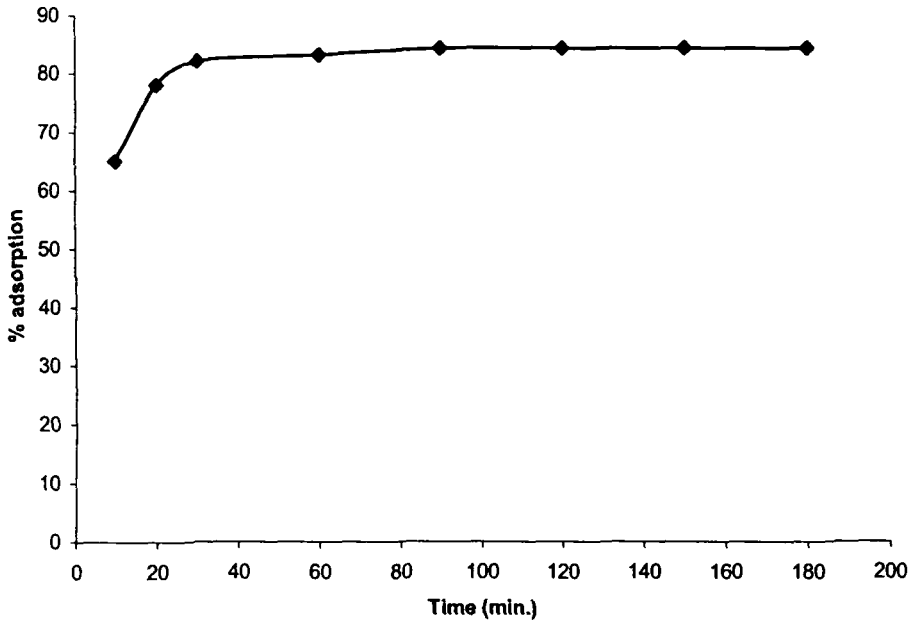


Figure 5.1. Effect of time of removal of arsenic(III) by activated carbon.

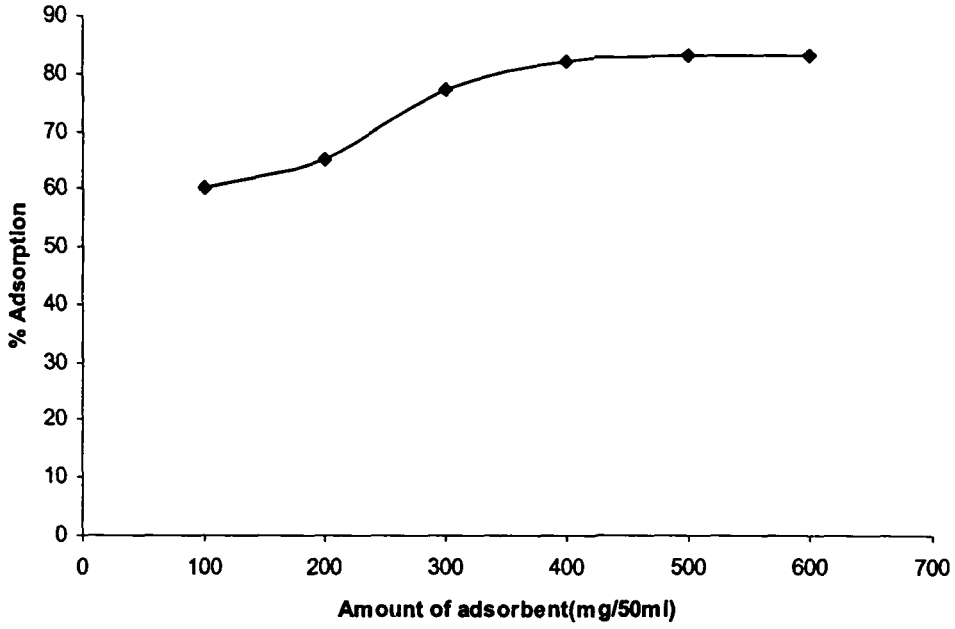


Figure 5.2. Effect of activated carbon dose on the adsorption process.

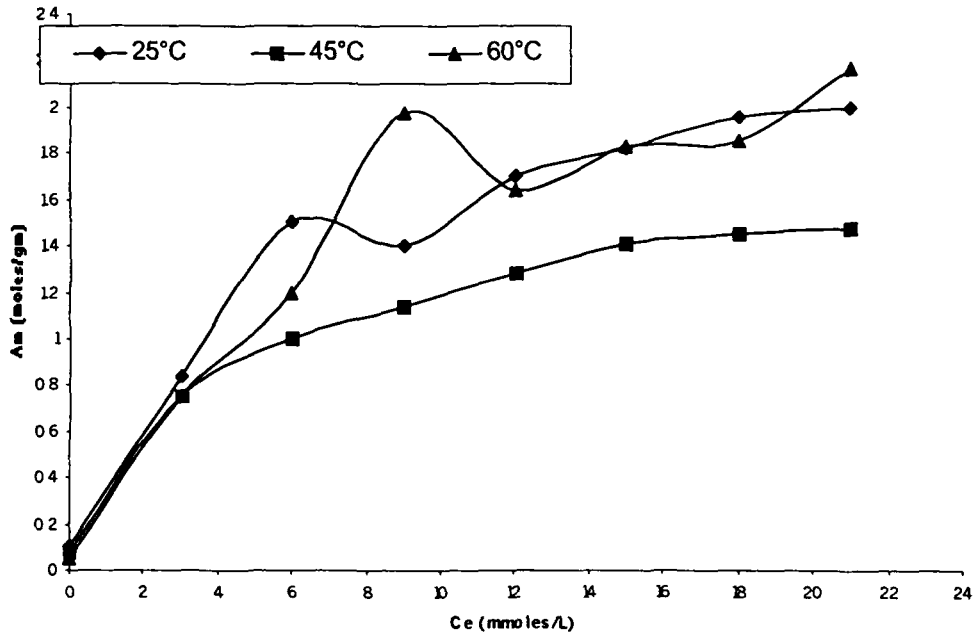


Figure 5.3. The adsorption of Arsenic(III) on activated carbon at different temperatures in aqueous medium.

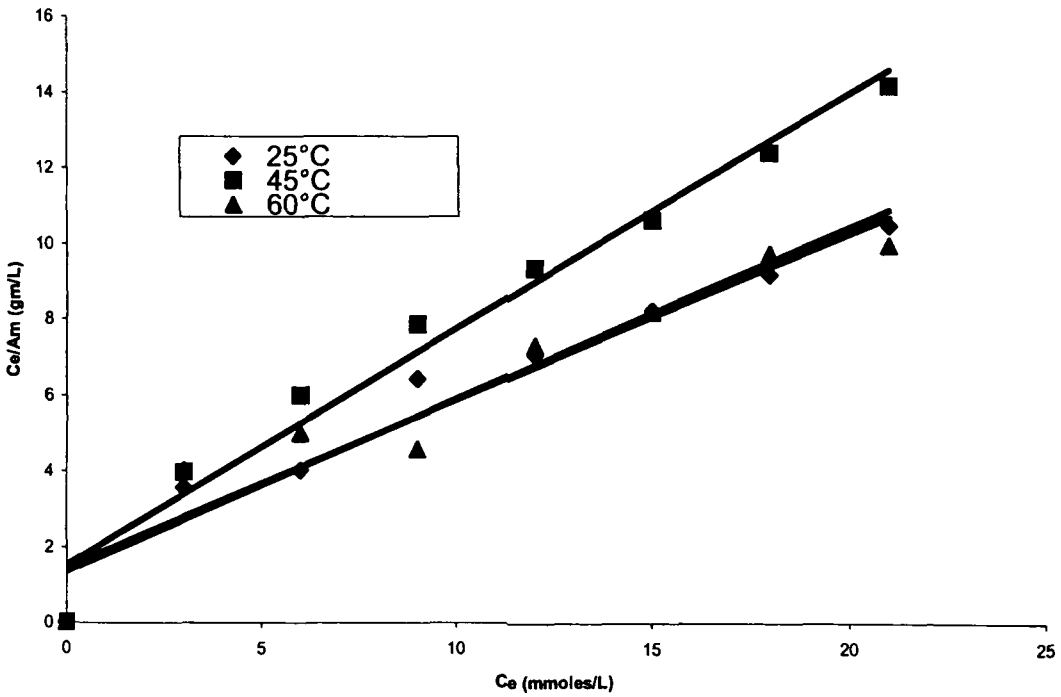


Figure 5.4. Langmuir plots for the adsorption of Arsenic(III) on activated carbon in aqueous medium.

TABLE-5.3

Related parameters for the adsorption of arsenic(III) on activated carbon in aqueous medium at different temperatures

Temp.	Reg. Coeff.	Langmuir Constant		Reg. Coeff.	Freundlich Constant	
(^{0}C)	(R)	K	b	(R)	K	1/n
25	0.98	0.34	2.19	0.76	0.27	0.31
45	0.99	0.41	1.60	0.74	0.22	0.30
60	0.96	0.30	2.28	0.74	0.18	0.38

Langmuir and Freundlich isotherms are listed in Table 5.3. Isotherm at 25°C and 45°C shows L_2 type isotherm and are sigmoid, and isotherms at 60°C shows steep rise in adsorption isotherm, which is of the L_3 type. The adsorption of arsenic(III) does not show a regular increasing or decreasing trend in any of the concentration of arsenic(III) in the temperature range studied. The plateaus are obtained in the adsorption isotherm at 45°C owing to the formation of a complete monolayer of arsenic(III) on the surface of the activated carbon. A critical analysis of the adsorption isotherm in aqueous system reveals that the adsorption of arsenic(III) on the activated carbon increases with a rise in temperature form 45°C to 60°C. The total adsorption at 25°C shows an abnormal value, this anomaly may be interpreted in terms of an increased adsorbate-adsorbent interaction and steep rise in the adsorption isotherm at above 60°C. This may be due to the chemisorptions of arsenic(III) species on the activated carbon surface. The rise in temperature increases the surface activity as well as saturation value.

THERMODYNAMIC STUDIES

The various thermodynamic parameter like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) associated with the adsorption of arsenic(III) ions on to the activated carbon were determined by using the equations, (3), (4), and (5). All the thermodynamic parameters are calculated and listed in Table 5.4. Heat of adsorption (ΔH), which indicates the mechanism of adsorption, was calculated by equation (4). A plot of ln k versus 1/T yields a straight line with slope $-\Delta H/R$ as

TABLE-5.4

Thermodynamic parameters for the adsorption of arsenic(III) on activated carbon in aqueous medium at different temperatures

Temp.	Langmuir Adsorption Isotherm				Freundlich Adsorption Isotherm			
(^{0}C)	lnK	ΔG	ΔS	ΔH	lnK	ΔG	ΔS	ΔH
25	-1.08	2.677	-0.017	-2.0316	-1.296	3.212	-0.043	-9.575
45	-0.89	2.356	-0.015		-1.498	3.962	-0.042	
60	-1.20	3.323	-0.016		-1.705	4.722	-0.043	

ΔG = kJmole^{-1}, ΔS = kJmole^{-1}K^{-1}, and ΔH = kJmole^{-1}

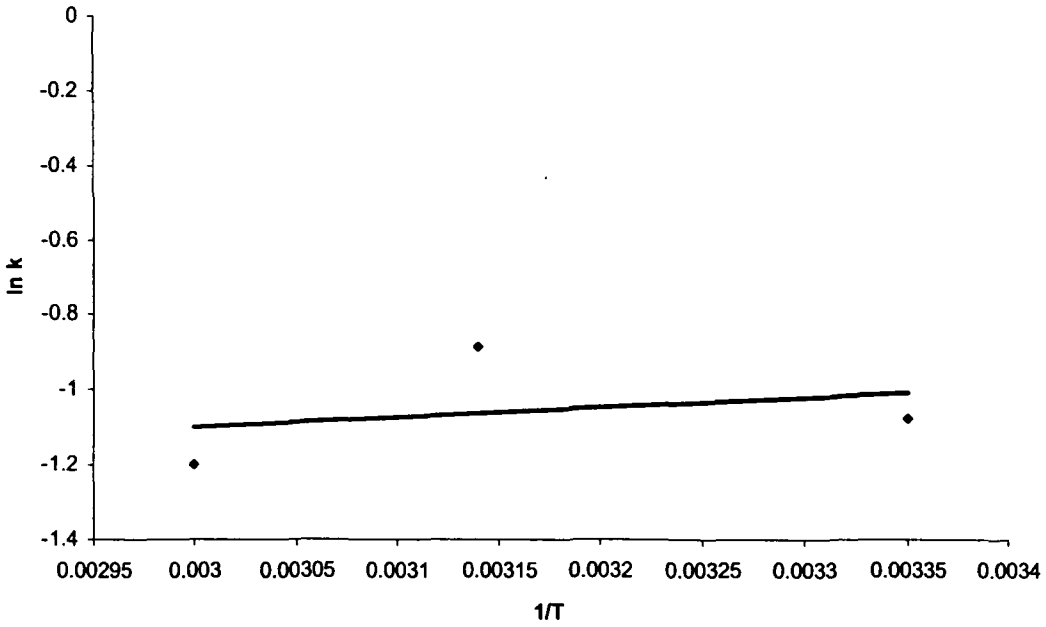


Figure 5.5. The plot of Langmuir constant (ln k) versus 1/T.

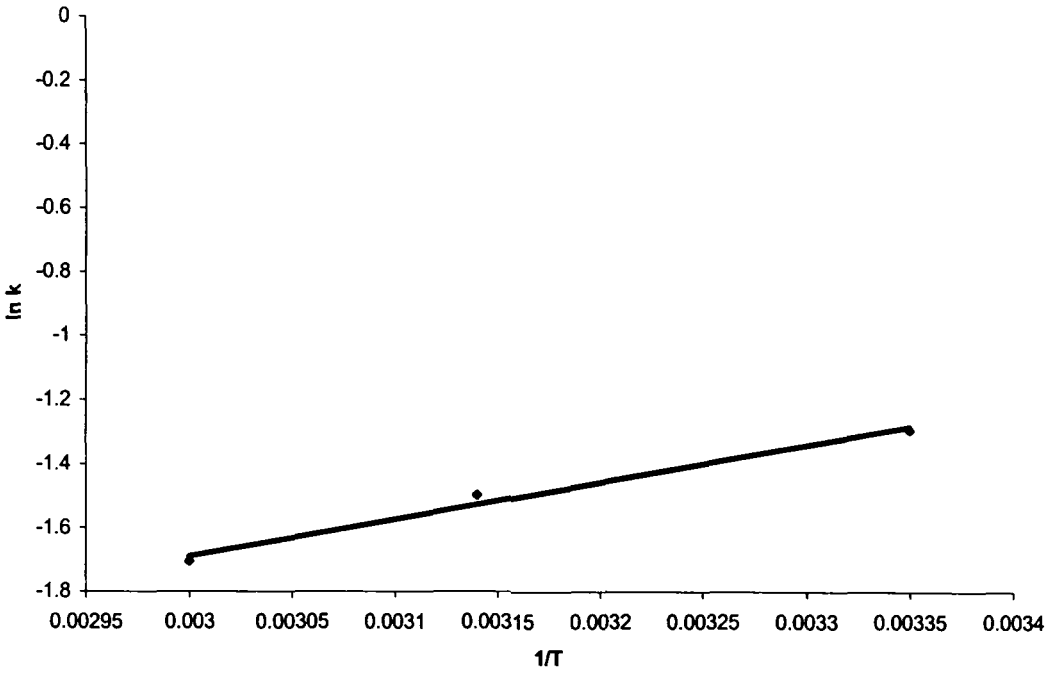


Figure 5.6. The plot of Freundlich constant (ln k) versus 1/T.

shown in Figure 5.5 and 5.6. The ΔH values were found to -2.316 kJ/mole for Langmuir isotherm and -9.575 kJ/mole for Freundlich isotherm. The negative value of ΔH indicates the process is exothermic also the process may be due physical in nature and can be easily reversed by supplying the heat equal to calculated ΔH value to the adsorption system. Moreover, the negative values of ΔS in Langmuir isotherm point out the spontaneity in the adsorption process with reduction in molecular size and increased randomness at solid liquid interface.

REFERENCES

1. National research council. *Arsenic in drinking water.* Washington, DC: National Academy Press; (1999).
2. J. C. Saha, A. K. Dikshit, M. Bandyopadhyay and K. C. Saha, *Crit. Rev. Environ. Sci. Technol.*, **29(3)**, 281 (1999).
3. F. W. Pontius, K. G. Brown, C-J Chen, *J. Am. Water Works Assoc.*, **86(9)**, 52 (1994).
4. World Health Organization Environmental Health Criteria, 18, arsenic, WHO, Geneva, Switzerland, p.1774, (1981).
5. J. E. Fergusson, *The heavy elements: Chemistry, Environmental impact and health effects*, Pergamon Press, Oxford, and p.551 (1990).
6. M. R. Jekel, *Removal of arsenic in Drinking water treatment.* In: Jerome O. Nriagu editor. Arsenic in the Environment, Part I: Cycling and Characterization. New York: Wiley, **1994**.
7. E. O. Kartinen Jr, Martin CJ. *An overview of arsenic removal processes.* Desalination, **103**, 78 (1995).
8. M. J. Bitner, J. D. Chwirka. Proceedings of 39th New Mexico Water Conference, Albuquerque, N. M., p. 251-55 (1994).
9. V. P. Simeonova, *Water Supply*, **18(1/2)**, 636 (2000).
10. P. B. Nagarnaik, A. G. Bhole and G. S. Nagarajan, *Int. J. Environ. & Pollut.*, **19(2)**, 177 (2003).

11. C. Raji and T. S. Anirudhan, *J. of Scientific and ind. Res.*, **57(1)**, 10 (1998).

12. F. Ferrero and M. P. G. Paratii, *Ann. Chim*, **86**, 125 (1996).

13. D. Gosawami and A. K. Das, *Int. J. Water*, **1(1)**, 61 (2000).

14. P. B. Nagarnaik, A. G. Bhole and G. S. Nagarajan, *Journal of Ecotoxicology & Environmental Monitoring*, **14(2)**, 93 (2004).

15. N. Khalid, S. Ahmad, A. Toheed and J. Ahmad, *Adsorpt. Sci. and Technol.*, **16(8)**, 655 (1998).

16. G. N. Manju, C. Raji and T. S. Aniruthan, *Water Res.*, **32(10)**, 3062 (1998).

17. H. J. Min, *Diss. Abst. Int.*, **58(10)**, 5574 (1998 B).

18. M. Tominaga and H. Ishida, *Eco. Ind.*, **5(9)**, 25 (2000).

19. S. Shevade, R. Ford, P. Kaiser and J. Wilson, *ACS, Division of Environmental Chem.*, **43(2)**, 367 (2003).

20. R. Klipper, A. Schlegel, W. Podszun and R. Scidel, *PCT Int. Appl*, 32pp (2003).

21. M. Abe, Y. Tanaka and M. Tsuji, *Ion Exch. Adv. Proc. IEX*, **92**, 326 (1992).

APPENDIX

1. Measurement of specific surface area

Gas adsorption method

The amount of gas adsorbed on the surface of a powder sample is measured as a function of the pressure of the adsorbate gas, and is used to determine the specific surface area of a powder sample. Measurements are usually performed at the boiling point of liquid nitrogen (-196°C). The following relationship holds for the physio sorption of gas by the powder sample, when $P/P\circ$ is in the range of 0.05 to 0.30 for pressure P of the adsorbate gas in equilibrium for the volume of gas adsorbed, Va

$$1/Va(Po/P-1)=(C-1)/VmC\times P/Po+1/VmC$$

Where

P: Partial vapour pressure of adsorbate gas in equilibrium (kPa)

Po: Saturated pressure of the adsorbate gas at -196°C (kPa)

Va: Volume of gas adsorbed at equilibrium (ml)

Vm: Volume of gas adsorbed in a monolayer (ml)

C: Dimensionless constant related to the enthalpy of adsorption and condensation of the adsorbate gas

The specific surface area, S, is determined from Vm, the volume of gas adsorbed in a monolayer on the sample.

$$S=Vm\times N\times\alpha/m\times 22400$$

Where

S: Specific surface area (m^2/g)

N: Avagadro constant

α: Effective cross-sectional area of one adsorbate molecule (m^2)

m: Mass of the test powder (g)

Specific surface area is generally expressed in units of m^2/g.

Method 1: Dynamic flow method

In the dynamic flow method, a mixture of the adsorbate gas and a carrier gas is passed over a sample, and the volume of gas adsorbed is determined from the change in the concentration of the adsorbate gas in the mixture before and after the exposure to the powder sample. Nitrogen is typically used as the adsorbate gas, and a gas such as krypton

is preferred for samples with a small specific surface area. Helium is generally used as the diluents gas.

Method 2: Volumetric method

In the volumetric method, the test powder is placed in a sample container with a known volume and the volume of gas adsorbed is determined from the change in pressure associated with the adsorption of gas on the surface of sample powder. Nitrogen is typically used as the adsorbate gas, and a gas such as krypton is preferred for samples with a small specific surface area.

Atomic absorption spectroscopy

Atomic absorption spectrometry is analytical techniques that measure the concentrations of elements. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level.

Light source – Hollow cathode lamps

A hollow cathode lamp is used as the radiation source to excite the free atoms in the flame. The hollow cathode lamp produces a narrow spectral line characteristic of the material of the cathode and the fill gas neon or argon. The hollow cathode and ring anode are enclosed in a glass envelope, filled with either argon or neon at a reduced pressure of 7.5 mBar (10 torr). A potential of 150-400 volts is applied to the electrodes, which causes the fill gas to ionize. The gas ions are accelerated by the applied potential, and collide with the cathode releasing a cloud of atoms from the cathode. These atoms are further excited by collisions with gas ions to a high-energy state. Characteristic wavelength is then emitted by the atoms as they fall to the ground state.

Atomization

For atomic absorption to occur, the atoms have to be introduced into the excitation beam as "free" atoms. Analysis is normally conducted from a solution in which the atoms are chemically bonded and solvated. To form free atoms, the solvent has to be removed and the chemical bonds broken to form free atoms. This is generally done in one of three ways:

(i) By a chemical flame

(ii) By flameless heating

(iii) By hydride generation

Flame atomization

The flame atomizer consists of three major components, a nebulizer, a spray chamber and a burner. The overall system has to convert the liquid into an aerosol, select the correct droplet size and transfer the sample to the burner, where atom formation occurs. This is principally the heart of an atomic absorption system.

Nebulizer

The nebulizer used in atomic absorption is the pneumatic type in which the flow of gasses through the orifice creates a vacuum drawing the sample up into the capillary. As the solution passes through the venturi an aerosol is formed. The impact bead at the end of the nebulizer is used to produce a greater proportion of small particles, which are easier to atomize.

Spray chamber

The spray chamber acts as a classifier to remove large particles and supply a constant feed of fine particles to the burner, considerable noise will be seen and the flame temperature reduced. For optimum sensitivity, particles of a consistent size (less than 10μm) should reach the burner.

Burners

A laminar flow premix burner with a long path length is used in atomic absorption. Materials to minimize sample contamination are used in its construction. The GBC burners are of all titanium construction for robustness, stability and inertness.

Two types of flame are commonly used, the properties of these two flames are:

Air-acetylene flame

This is the most widely used flame in atomic absorption spectroscopy, with most elements showing best sensitivity in the stoichiometric flame. Four easily distinguishable flames are used:

(i) Oxidizing flame (lean) – a very stiff flame with small inner blue cone.

(ii) Stoichiometric flame – a stiff flame with bigger blue cone and an almost luminous appearance.

(iii) Luminous flame – as the name suggests the flame is luminous, however the blue cone is still prominent.

(iv) Reducing flame (rich) – extremely luminous flame almost sooty at the top.

The temperature of this flame is approximately 2300°C and is not hot enough for elements forming refractory oxides.

Nitrous oxide-acetylene flame

This is much hotter (approximately 2900°C) and faster burning flame and should only be used with a nitrous oxide-acetylene burner. A larger range of refractory elements can be analysed with this flame, due to the higher temperature and strongly reducing nature. A nitrous oxide-acetylene flame has three distinct zones:

(i) An initial combustion zone whiteish-blue in colour

(ii) A secondary interconal zone red-pink in colour (normally called a red feather)

(iii) A blue diffusion zone

Flameless electro-thermal atomization

In this method the nebulizer, spray chamber and burner are replaced by an electrically heated carbon furnace.

The graphite furnace by virtue of its small size ensures a large population of "free" atoms in the optical path and requires extremely small volumes of samples, typically 2-50µl. Due to the greater efficiency of the furnace the sensitivity is greater by 10-200 times depending on the elements.

The graphite furnace power supply applies power to the furnace in ten steps. Each step can be programmed for three parameters:

(i) Final temperature.

(ii) Ramp time.

(iii) Hold time.

Monochromator

In atomic absorption spectroscopy a monochromator of high resolution is not essential. A medium resolution monochromator capable of 0.2 nm resolution is quite adequate. The resolution of a monochromator (the minimum repeatable band pass) depends on a variety of factors such as focal length, number of lines per millimeter on the grating and the width of the entrance and exit slits. For atomic absorption spectroscopy the most common slit sizes used are 0.2, 0.5 and 1.0 nm.

Detector read out

A photomultiplier tube is almost exclusively used in atomic absorption as the detector. This could be a narrow response type such as a HAMAMATSU R106 tube whose peak response is in the range of 185 to 500 nm, although it can be used for wavelengths of up to 700 nm. More common however is the use of wide range of photomultiplier tubes with peak response of 185 to 850 nm, thereby eliminating the need to change photomultiplier tubes.

A GBC 932 atomic absorption spectrometer, Australia with hydride generation facility operating with an air-acetylene flame was used to analysis the metal ions with the following instrumental conditions:

For Zn(II) ion:- wave length = 213.9 nm; background correction = yes; lamp current = 5.0 mA; slit width = 0.5 mm.

For Cd(II) ion:- wave length = 228.8 nm; lamp current = 3.0 mA; slit width = 0.5 mm.

For Cu(II) ion:- wave length = 324.7 nm; lamp current = 3.0 mA; slit width = 0.5 mm.

For Pb(II) ion:- wave length = 217.0 nm; background correction = yes; lamp current = 4.0 mA; slit width = 1.0 mm.

For Ni(II) ion:- wave length = 341.5 nm; lamp current = 4.0 mA; slit width = 0.2 mm.

For Cr(III) ion:- wave length = 357.0 nm; lamp current = 6.0 mA; slit width = 0.2 mm.

For As(III) ion:- graphite furnace facility, matrix modifier = nickel nitrate; wave length = 193.7 nm; background correction = yes; lamp current = 8.0 mA; slit width = 0.5 mm.

2. TABLE A 1

Various physical parameters for the adsorbents (Mango wood and Sissoo wood)

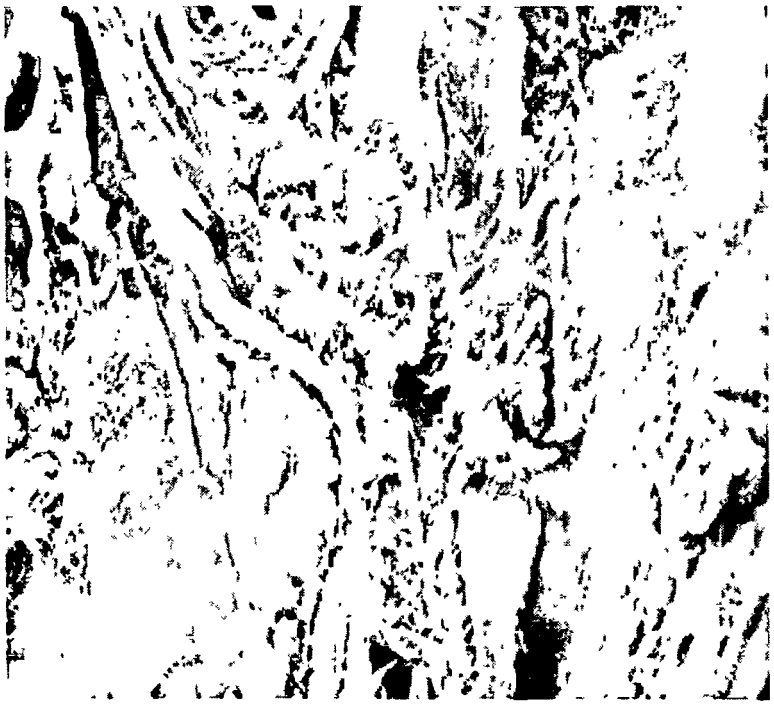
Parameters	Values	
	Mango wood	**Sissoo wood**
pH (aqueous solution)	7.05	7.10
Particle size (mesh)	30-50	30-50
Surface area (m^2/g)	543.25	677.00
Bulk Density (g/cm^3)	0.32	0.26
Moisture contents (%)	6.35	5.85

The specific surface area of wood sawdusts was determined by applying BET (volumetric method) using a gas mixture of 30% N_2/ Ar.

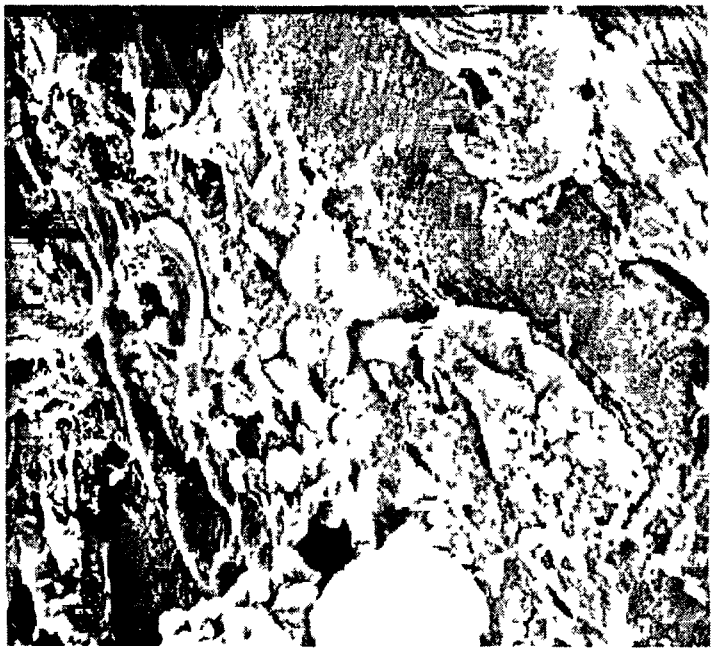
The cell walls of sawdust mainly consist of cellulose and lignin and many hydroxyl groups, such as tannins or other phenolic compounds. Lignin is a polymer material built up from the phenyl propane nucleus, an aromatic ring with a three-carbon side chain. Vanillin and syringaldehyde are the two other basic structural units of lignin molecule. Tannins are complex polyhydric phenols, which are soluble in water and have the property of precipitating protein (gelatin).

On page 89, the specific surface area of the sawdust mentioned as 0.77 m^2/g is a typographical mistake and it is 677.0 m^2/g.

SEM Photograph

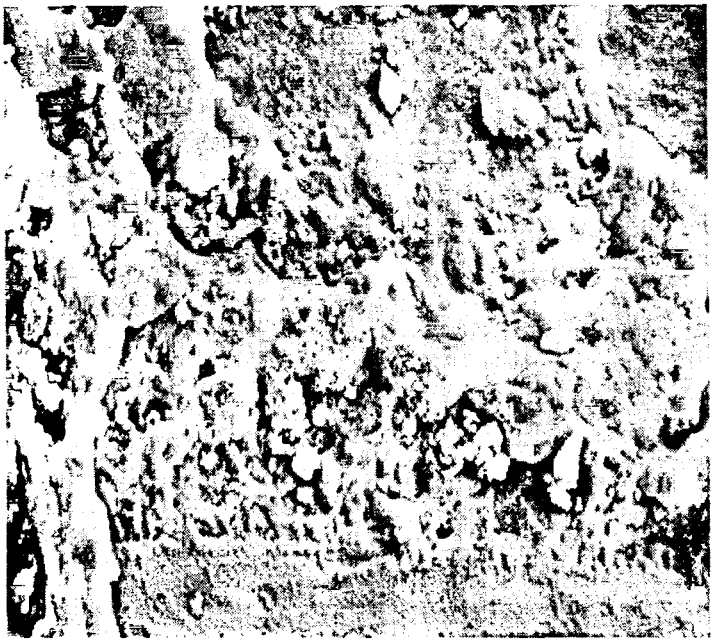


SEM image (Mag: x 5000) of sawdust of Dalbergia sissoo



SEM ımage (Mag: x 5000) of sawdust of Mangıfera ındıca

SEM image (Mag: x 5000) of activated carbon



SEM image (Mag: x 5000) of fly ash

3. In chapter 2, the sissoo wood sawdust was treated with 2% formaldehyde in the ratio of 1:3 (sawdust: formaldehyde, w/v) at 50°C for 6 hrs to immobilize the water-soluble substances. The sissoo wood sawdust was filtered and washed with distilled water to remove free formaldehyde and activated at 105°C in oven for 24 hrs. To enhance the capability and efficiency of sawdust adsorption, pre-treatment of sawdust may be needed. In chapter 3, the mango wood sawdust was treated with dilute HCl to remove the adhering dust and other adsorbed inorganic species. It was washed several times with distilled water until the effluent was free from chloride ion and then activated at 105°C in oven for 24 hrs.

In chapter 4, all the three adsorbents were treated in a similar fashion for the sake of their comparison and to study their relative adsorption behavior.

4. All the experiments were run in triplicate and the mean of the observations are shown in figures and tables and used in calculation through out the thesis.

The software developed in FORTRON in our laboratory is used for thermodynamic calculations. The program employees the Least Squares Method for the regression analysis for fitting of the data in Freundlich and Langmuir adsorption models as well as for calculation of thermodynamic parameters.

The listing of the program is enclosed in annexure-I.

In chapter 5, the straight-line plot running through the three measured data is because of van't Hoff equation where lnk versus 1/T was plotted. Since the study was done only at three temperatures so in the figures there are three points only. More points would have been possible only if the studies would have been done at more temperatures.

5. The studies of the kinetics of adsorption were carried out at room temperature (27 ± 2°C).

6. River sample was taken to study the effect of solution matrix on the adsorption of metal ions on different adsorbents. The concentration of the metal ions under study was adjusted in the natural river samples to 100 ppm by adding standardized solution of desired metal ions [Zn(II), Cd(II), Cu(II), Cr(III), Ni(II), Pb(II), and As(III)]solutions. The physicochemical analysis of river water is given in Table A 2.

TABLE A 2

Physicochemical analysis of river water

Temperature (°C)	28
pH	8.3
Turbidity (NTU)	15.0
EC (μmhos)	130.0
TSS (mg/L)	200.0
TDS (mg/L)	110.5
Acidity	---
Total alkalinity (mg/L)	85.0
Chloride (mg/L)	10.0
Sulphate (mg/L)	3.0
Phosphate (mg/L)	3.5
Sodium (mg/L)	4.0
Calcium (mg/L)	21.5
Magnesium (mg/L)	8.0
Dissolved oxygen (mg/L)	8.2
BOD (mg/L)	2.8
COD (mg/L)	8.4

The efficiency of removal of heavy metal ions from the above sample by the different adsorbents were tested using the optimized adsorption conditions and listed in Table A 3.

TABLE A 3

Removal of heavy metal ions

Chapters	Adsorbents	Metal ions	Removal (%)
Chapter 2	Treated sissoo wood sawdust	Zn(II)	68
		Cd(II)	65
Chapter 3	Mango wood sawdust	Cu(II)	76
		Cr(III)	75
		Ni(II)	73
		Pb(II)	72
Chapter 4	Fly ash	Cu(II)	29
	Sissoo sawdust		66
	Activated carbon		62
Chapter 5	Activated carbon	As(III)	64

ANEXURE-I

```
C       THE PROGRAM FOR THE ADSORPTION OF METAL IONS
C       F R E U N D L I C H AND L A N G M U I R AND B.E.T. Equation
C       ********************************************************
        CHARACTER*80 NAME(5),SUBHEAD*80,EQN(3)*20,HEAD*80,UNIT*10
        REAL X(10,5),Y(10,5),AT(5),TM(5),P(2),M(2),CI(10,5)
        INTEGER N(5)
        DATA EQN/'F R E U N D L I C H','L A N G M U I R','B.E.T'/
C       R=1.987          !CAL/K/MOL
C       UNIT='CAL/K/MOL'
        R=8.3147         !J/K/MOL
        UNIT='J/K/MOL'
        LOCK=0.0
        READ(5,*)NSYS
        DO 10 INS=1,2
        DO 10 II=1,NSYS
        READ(5,1)NAME(II)
        READ(5,*)AMM,CONC,VT,VOL,WT
        READ(5,*)AMM,VOL,WT
55      TYPE 1,NAME(II)
        WRITE(8,2)NAME(II)
2       FORMAT(1H1,,/5X,80('*'),/5X,A80,/5X,80('*'))
        HEAD=NAME(II)
        FORMAT(A80)
        WRITE(8,34)EQN(INS)
34      FORMAT(10X,'FITTING OF THE',A20,'EQUATION',/)
        READ(5,*)S,M(1),P(1),M(2),P(2),NTEMP
        READ(5,*)S,A1,A2,NTEMP
        READ(5,*)NTEMP
12      WRITE(8,*)S,M(1),P(1),M(2),P(2)
12      WRITE(8,*)S,A1,A2,NTEMP !TEMPORARILY
        DO 50 J=1,NTEMP
        READ(5,*)TM(J),N(J)
        READ(5,*)(X(I,J),I=1,N(J))       ! X---> EQUILIBRIUM CONCH.
        READ(5,*)(Y(I,J),I=1,N(J))       ! Y---> X/M
50      CONTINUE
        DO 50 I=1,N(J)
        X(I,J)=X(I,J)*20
        Y(I,j)=Y(I,J)*X(I,J)/100
        CI(I,J)=X(I,J)
        X(I,J)=X(I,J)-Y(I,J)*1E-4
        Y(I,J)=Y(I,J)*AMM*VOL/(1E3*WT)! Y=Y*VOL/(WT.*1000)*MOL.MASS
50      CONTINUE
        CALL TITER(X,Y,CI,N,TM,NTEMP,LOCK)
        CALL FREND(X,Y,N,NTEMP,TM,R,HEAD,UNIT)
        CALL LAGMUR(X,Y,N,NTEMP,TM,R,HEAD,UNIT)
        CALL BET(X,Y,CI,N,NTEMP,TM,R,HEAD,UNIT)
10      CONTINUE
        STOP
        END
        SUBROUTINE LSFIT(X,Y,CEPT,SLOPE,N)
        DIMENSION X(10),Y(10)
        SUMX=0.0
        SUMY=0.0
        SUMXY=0.0
        SUMXSQ=0.0
        DO 10 I=1,N
        SUMX=SUMX+X(I)
        SUMY=SUMY+Y(I)
        SUMXY=SUMXY+X(I)*Y(I)
        SUMXSQ=SUMXSQ+X(I)*X(I)
10      CONTINUE
        AN=N
        ANMUR=AN*SUMXY-SUMX*SUMY
        DENR=AN*SUMXSQ-SUMX*SUMX
        SLOPE=ANMUR/DENR
        CEPT=(SUMY-SLOPE*SUMX)/AN
        RETURN
        END
```

```
      SUBROUTINE SURCON(S,M,P,X,NN,CY)
      SUBROUTINE SURCON(S,A1,A2,X,NN,CY)
      REAL A(2),P(2),M(2),S,N,X(10),CY(10)
      N=6.023E23
      DO 10 I=1,2
10    A(I)=1.091E-16*((M(I)*1E24)/(N*P(I)))**(2/3)
      A1=A(1)*P(1)/M(1)
      A2=A(2)/(M(2)*1E6)
      DO 20 I=1,NN
      A3=S/(N*X(I))
      XX=A1/(A3-A2)
      CY(I)=LOG(XX)
      RETURN
      END
      SUBROUTINE RCOF(X,Y,N)
      REAL MSRG,MSRS
      DIMENSION X(20),Y(20)
      SUMX=0.0
      SUMY=0.0
      DO 1 I=1,N
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
1     CONTINUE
      XAV=SUMX/N
      YAV=SUMY/N
      SQDSQ=0.0
      SYDSQ=0.0
      SXYD=0.0
      DO 3 I=1,N
      SXDSQ=SXDSQ+(X(I)-XAV)**2
      SYDSQ=SYDSQ+(Y(I)-YAV)**2
      SXYD=SXYD+(X(I)-XAV)*(Y(I)-YAV)
3     CONTINUE
      AA=SXDSQ
      BB=SYDSQ
      CC=SXYD
      R=CC/(SQRT(AA*BB))
      B=CC/AA
      SSRG=CC*B
      SSRS=BB-SSRG
      MSRG=SSRG
      MSRS=SSRS/(N-2)
      F=MSRG/MSRS
      WRITE(8,20)R,F
      TYPE 20,R,F
20    FORMAT(/5X,45('*'),/5X,'THE STATISTICAL PARAMETERS ARE AS UNDER',
     1/10X,'R=',F7.5,3X,'F=',F10.5,/5X,45('*'))
100   CONTINUE
      RETURN
      END

      SUBROUTINE TITER(X,Y,CI,N,TM,NTEMP,LOCK)
      CHARACTER*80 NAME(5),SUBHEAD*80
      DIMENSION CM(20),TI(20),TF(20),X(10,5),Y(10,5),TM(5),N(5),CI(10,5)
      IF(LOCK.EQ.0)READ(5,*)AMM,CONC,VT,VOL,WT !AMM=MOL MASS, CONC=CON. OF
CATION
C     WT=WEIGHT OF ADSORBENT, VT=VOL. TAKEN, VOL=TOTAL VOL. OF SOLUTION
      IF(LOCK.EQ.0)WRITE(7,2)AMM,CONC,VT,VOL,WT
      LOCK=1.0
2     FORMAT(/5X,'MM OF CATION=',F6.2,/5X,'CONC=',F7.4,2X,'M'
     1/5X,'VOL TAKEN=',F5.2,'ML',/5X,'TOTAL VOL=',F5.2,'ML',/5X,
     1'WT=',F7.3,2X,'GM',/2X,60('-'),/)
      READ(5,*)NTEMP
      DO 251 J=1,NTEMP
      READ(5,*)TM(J),N(J)
      READ(5,1)SUBHEAD
1     FORMAT(A80)
      READ(5,*)(CM(I),I=1,N(J))
      READ(5,*)(TI(I),I=1,N(J))
```

```
      READ(5,*)(TF(I),I=1,N(J))
      DO 301 I=1,N(J)
      XM(I)=(TI(I)-TF(I))*AMM*CONC/WT
      Y(I,J)=(TI(I)-TF(I))*AMM*CONC/WT
      YC(I)=TF(I)*CONC*AMM/VOL
      CI(I,J)=TI(I)*CONC*AMM/VOL
301   CONTINUE
      WRITE(7,11)SUBHEAD
11    FORMAT(5X,80('-'),/5X,A80,/5X,80('-'),/)
      WRITE(7,311)
311   FORMAT(6X,'CONC OF M+ TITR.I TITR. II X/M',9X,'CE'
     1/6X,'(M MOLES) (ML) (ML) (MG/MG)',7X,'(MG/ML)',/2X,
     260('-'))
      DO 251 I=1,N(J)
      WRITE(7,511)CM(I),TI(I),TF(I),Y(I,J),X(I,J)
511   FORMAT(5X,4F10.5,2X,F12.7)
251   CONTINUE
      RETURN
      END

      SUBROUTINE FREND(X,Y,N,NTEMP,TM,R,HEAD,UNIT)
      CHARACTER*80 HEAD,UNIT*10
      DIMENSION X(10,5),Y(10,5),XX(10),YY(10),AT(5),CY(10),ECK(5),
     1TM(5),DG(5)
      INTERGER N(5)
      WRITE(8,2)HEAD
2     FORMAT(1H1,/5X,80('*'),/5X,A80,/5X,80('*'))
      WRITE(8,1)'FITTING OF F R E U N D L I C H EQUATION'
1     FORMAT(/5X,45('*'),/5X,A45,/5X,45('*'))
      DO 20 J=1,NTEMP
      AT(J)=TM(J)+273
      DO 30 I=1,N(J)
      XX(I)=LOG(X(I,J))
      YY(I)=LOG(Y(I,J))
30    CONTINUE
      WRITE(8,4)TM(J)
4     FORMAT(15X,'STUDIES AT',F7.2,'DEGREES CELCIUS'
     1//75('-'),/4X,'X/M',13X,'C',12X,'IN X/M',5X,'LN C',8X,
     2'LN X/M(MOD)',/75('-'))
      NN=N(J)
      CALL LSFIT(XX,YY,CEPT,SLOPE,NN)
      DO 40 I-1,N(J)
      CY(I)-XX(I)*SLOPE+CEPT
      CALL SURCON(S,M,P,X,N,CY)
      CALL SURCON(S,A1,A2,X,N,CY)
      EY(I)=CY(I)-XX(I)
      TYPE 3,Y(I,J),X(I,J),YY(I),XX(I),CY(I)
      WRITE(8,3)Y(I,J),X(I,J),YY(I),XX(I),CY(I)
      WRITE(6,88)XX(I),YY(I),CY(I)
      WRITE(6,*)XX(I),YY(I)
88    FORMAT(3F10.5)
3     FORMAT(2X,5(E12.6,2X),7X,F8.4)
40    CONTINUE
      WRITE(8,44)CEPT,SLOPE
44    FORMAT(//15X,'LN X/M=',F10.5,'+',F7.5,'LN C'//)
      CALL LSFIT(XX,YY,CEPT,SLOPE,NN)
      ESK(J)=CEPT
      TYPE*,CEPT,ESK(J),R
      CALL RCOF(XX,YY,NN)
      TYPE*,CEPT,ESK(J),R,AT(J)
      DG(J)=-1.0*R*AT(J)*ESK(J)
      DG(J)=DG(J)/1000          !VALUE IS CHANGED INTO KILO
      AK=10**(CEPT/2.303)
      WRITE(8,5)CEPT,AK,SLOPE
      TYPE 5,CEPT,AK,SLOPE
5     FORMAT(/2X,'LN K=',E12.5,2X,'K=',E12.5,'1/N=',F8.5,/,50('-'),/)
20    CONTINUE
      IF(NTEMP.EQ.1)RETURN
      WRITE(8,33)HEAD
33    FORMAT(1H1,//5X,'THE THERMODYNAMIC PARAMETERS FOR',/5X,A80,
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```
      1/5X,80('-'),//9X,'TEMP(C)',5X,'LN KO',10X,'/\GO',8X,'/\SO',
      1/37X,'__',10X,'__',5X,80('-'))
       CALL HEAT(ECK,AT,NTEMP,R,DG,UNIT)
       RETURN
       END

       SUBROUTINE LAGMUR(X,Y,N,NTEMP,TM,R,HEAD.UNIT)
       CHARACTER*80 HEAD,UNIT*10
       DIMENSION X(10,5),Y(10,5),XX(10),YY(10),AT(5),CY(10),ECK(5),TM(5),DG(5)
       INTEGER N(5)
       WRITE(8,2)HEAD
2      FORMAT(1H1,/5X,80('*'),/5X,A80,/5X,80('*'))
       WRITE(8,1)'FITTING OF L A N G M U I R EQUATION'
1      FORMAT(/5X,45('*'),/5X,A45,/5X,45('*'))
       DO  50 J=1,NTEMP
       AT(J)=TM(J)+273
       DO 31 I=1,N(J)
       XX(I)=X(I,J)
       YY(I)=X(I,J)/Y(I,J)
31     CONTINUE
       NN=N(J)
       CALL LSFIT(XX,YY,CEPT,SLOPE,NN)
       B=1.0/SLOPE
       WRITE(8,41)TM(J)
41     FORMAT(15X,'STUDIES AT',F7.2,'DEGREES CELCIUS'
      1/50('-'),/8X,'X/M',12X,'C',9X,'C/(X/M)',5X,'C',9X,
      2'C/(X/M)[MODIFIED]',/50('-'))
       DO 42 I=1,N(J)
       CY(I)=XX(I)*SLOPE+CEPT
       TYPE 32,Y(I,J),X(I,J),YY(I),XX(I),CY(I)
       WRITE(8,32)Y(I,J),X(I,J),YY(I),XX(I),CY(I)
       WRITE(7,*)XX(I),YY(I)
32     FORMAT(2X,5(E12.6,2X))
42     CONTINUE
       CALL RCOF(XX,YY,NN)
       BK=SLOPE/CEPT
       IF(BK.LT.0) GO TO 52
       ECK(J)=LOG(BK)
       DG(J)=-R*AT(J)*ECK(J)
       DG(J)=DG(J)/1000        !VALUE IS CHANGED INTO KILO    .
       WRITE(8,51)BK,ECK(J),SLOPE,B
       TYPE 51,BK,ECK(J),SLOPE
51     FORMAT(/2X,'K=',F12.5,2X,'LN
K=',E20.9,'1/B=',F10.5,'B=',F10.5,/,50('-'),/)
       GOTO 50
52     WRITE(8,53)BK
53     FORMAT(5X,'THE LOG OF BK(',F12.5,') IS NOT POSSIBLE')
50     CONTINUE
       IF(NTEMP.EQ.1)RETURN
       WRITE(8,33)HEAD
33     FORMAT(1H1,//15X,'THE THERMODYNAMIC PARAMETERS FOR',/5X,A80,
      1/5X,80('_'),//10X,'TEMP(C)',5X,'LN KO',9X,'/\ GO',8X,'/\SO',
      1/37X,'__',10X,'__',/5X,80('-'))
       CALL HEAT(ECK,AT,NTEMP,R,DG,UNIT)
       RETURN
       END

       SUBROUTINE HEAT(ECK,AT,NTEMP,R,DG,UNIT)
       CHARACTER*10 UNIT
       DIMENSION ECK(5),AT(5),DS(5),TA(5),T(5),CECK(5)
       DO 20 J=1,NTEMP
       T(J)=1.0/AT(J)
20     TA(J)=T(J)*1.0E3
       IF(NTEMP.EQ.2)THEN
       A1=ECK(2)/ECK(1)
       A2(T(1)-T(2))/H
       DH=A1/A2
       ELSE
       CALL LSFIT(TA,ECK,CEPT,SLOPE,NTEMP)
       DH=-1.0*R*SLOPE
```

```
        ENDIF
        DO 100 J=1,NTEMP
        CECK(J)=TA(J)*SLOPE+CEPT
        DS(J)=(DH-DG(J))*T(J)
        WRITE(8,33)AT(J),ECK(J),DG(J),DS(J)
        TYPE 33,AT(J),ECK(J),DG(J),DS(J)
100     CONTINUE
33      FORMAT(5X,4F12.5)
        WRITE(8,200)
200     FORMAT(//10X,'THE PLOT OF LN K VERSUS 1/T X 1E+3',/10X,
       1'LN K 1/T X E3 (LN K) MOD',/5X,35('-'))
        DO 202 J=1,NTEMP
        WRITE(8,201)ECK(J),TA(J),CECK(J)
201     FORMAT(5X,3F12.5)
202     CONTINUE
        WRITE(8,44)DH,UNIT
        TYPE 44,DH,UNIT
44      FORMAT(2X,'THE ENTHALPY OF THE OVER ALL SYSTEM AT THE'
       1'TEMPERATURE RANGE STUDIED IS',//2X,'HO=',F15.8,'K',A10)
10      CONTINUE
        RETURN
        END

        SUBROUTINE BET(X,Y,CI,N,NTEMP,TM,R,HEAD,UNIT)
        CHARACTER*80 HEAD,UNIT*10
        REAL
X(10,5),Y(10,5),CI(10,5),ECK(5),ZX(10),ZY(10),ZCY(10),DG(5),AT(5),TM(5)
        INTERGER N(5)
        WRITE(8,2)HEAD
2       FORMAT(1H1,A80)
        DO 20 J=1,NTEMP
        AT(J)=TM(J)+273
        DO 10 I=1,N(J)
        ZX(I)=X(I,J)/CI(I,J)
        TYPE*,X(I,J),Y(I,J)
        A=(1-ZX(I))*Y(I,J)        !A=(1-Z)AM
        ZY(I)=ZX(I)/A             !ZY=Z/[(1-Z)AM]
10      CONTINUE
        WRITE(8,41)TM(J)
41      FORMAT(15X,'STUNDIES AT',F7.2,'DEGREES CELCIUS'
       1/50('-'),/4X,'X/M',8X,'C',6X,'Z/[(1-Z)AM]',5X,'Z',6X,
       2'Z/[(1-Z)AM] [MOD]',/,50('-'))
        NN=N(J)
        CALL LSFIT(ZX,ZY,CK,SLOPE,NN)
        DO 15 I=1,N(J)
        ZYC(I)=ZX(I)*SLOPE+CK
        WRITE(8,1)Y(I,J),X(I,J),ZX(I),ZY(I),ZCY(I)
1       FORMAT(2X,5F12.5)
15      CONTINUE
        CALL RCOF(ZX,ZY,NN)
        C=(SLOPE/CK)-1.0          !SLOPE=(C-1)/K, CK=1/K
        BK=1.0/CK                 !BK=K
        B=BK/C                    !B=(AM)MONO
        IF(BK.GT.0)THEN
        ECK(J)=LOG(BK)
        DG(J)=-R*AT(J)*ECK(J)
        DG(J)=DG(J)/1000          !VALUE IS CHANGED INTO KILO'S
        WRITE(8,5)ECK(J),BK,B,SLOPE
5       FORMAT(5X,'LN K=',F10.5,2X,'K=',F10.5,2X,'(AM)MONO=',F10.5,2X,
       1'(C-1)/K=',F10.5)
        ELSE
        WRITE(8,*)'UNABLE TO CALCULATE LN K, K=',BK
        ENDIF
20      CONTINUE
        CALL HEAT(ECK,AT,NTEMP,R,DG,DS,DH,UNIT)
        RETURN
        END
```

ITEMIZED CORRECTIONS

S. N.	Examiner comments	Corrections
1	The author might have been better discussed the techniques of measuring the specific surface area.....	Appendix
2	The author should present some basic physicochemical characteristics of these adsorbent.....	Appendix
3	A thorough and convincing explanation ought to be offered, why the sissoo wood sawdust was pretreated.....	Appendix
4	The author never says a single word about a number of the measurement repetitions.....	Appendix
5	The author writes: the studies of the kinetics of adsorption were carried out at room temp.....	Appendix
6	It is not good that the author does not report in his thesis any adsorption results obtained from the natural samples of the river.....	Appendix
7	The author should be more careful in the future, when citing the names of the reference authors.....	Corrected in reference list in chapter 1